On the elevation of the Boiling point of Aqueous Solutions of Electrolytes.

Part (1).

An improvement in the method of determining elevation. (Proc. of the Royal Society.)

Part (2).

Conductivity measurements at the Boiling point. An improved method. Instruments stretched.

Part (3).

Determination of the so called boiling point constant, and Molecular Weight determinations.

Part (4).

Concentrated Solutions, Hydration, Valency of Ions.

I wish to say that the work
on account of which is given
in the accompanying paper
was carried out by myself,
under the kindly guidance
of Professor MacGregor.

L. M. Johnston.

1 Argyle Place
Edinburgh

10th January 1906.

It has been pointed out* that error in Barometric readings might have had something to do with the high values obtained for the elevation of the boiling point constant.

To test this I set up two similar boiling point apparatus. The gas pressure was equalised by the use of a three way tube, and two bunsen burners exactly the same were used. The strength of the source of heat was therefore the same for each tube. The quantity of solvent used for each was 25 C.C.S. The one tube was used for solutions, the other for solvent. The readings in each instance were taken from Beckmann thermometers reading to one hundredth of a degree. In this way it was possible to obtain a thermal register of the change of atmospheric pressure during the observation of boiling point elevations.

For a series of experiments readings were taken of the barometer, the boiling point of the solvent and of solutions of Sodium Bromide. The observed boiling temperatures of Solutions were then corrected by the readings of the Barometer, and the Thermometer in the tube containing the solvent.

The following are the corrected readings.

By Barometer	2.320,	2.435,	2.525,	2.888.	
" Thermometer	2.320,	2.435,	2.527,	2.888.	
" Barometer	3.179,	3.631,	4.036,	4.405.	
" Thermometer	3.179,	3.629,	4.034,	4.403.	
" Barometer	4.866,	4.876,	4.892,		
" Thermometer	4.868,	4.874,	4.890,		

These figures only indicate a slight difference between Barometric and Thermal corrections. It would not therefore seem that error in /

*Proc. Royal Soc. Edin. XXV part II, page 965. (Paper herewith).

in Barometric corrections was responsible for the variations in the so called boiling point elevation constant which have been noticed. This is made more apparent by the fact that during the series of experiments given the value of C. (Boiling pt elev. Const) had increased on the basis of either correction by fully twenty five per cent.

I have pointed out* that the boiling point of the solvent was liable to be in error by one or two hundredths of a degree. It was also stated** that the high values obtained for the boiling point elevation constant in very dilute solutions were due to error in the determination of the boiling point of water. These statements taken together mean, that the observed boiling point of the solvent was liable to be too low by one or two hundredths of a degree. Consequently this error would be diminished by increasing the strength of the source of heat. This conclusion is in harmony with what Biltz and Luther*** say.

*1Biltz says "For the attainment of exact temperature adjustment it is necessary to maintain an extremely energetic boiling when water is used as solvent." **2Luther quoted by Biltz. "Finds it indispensible to maintain an energetic, and indeed stormy boiling, for the better adjustment of temperature." Each of these experimenters without tracing the cause has indicated the best experimental method of overcoming what was long a difficulty.

But in dealing with dilute aqueous solutions if this method only were employed erratic results in a less or greater degree would be obtained, because the rate of heat supplied to the solvent might be overdone or underdone. Overheating could also happen with solutions indeed stormy boiling of these would be practically certain to bring it on.

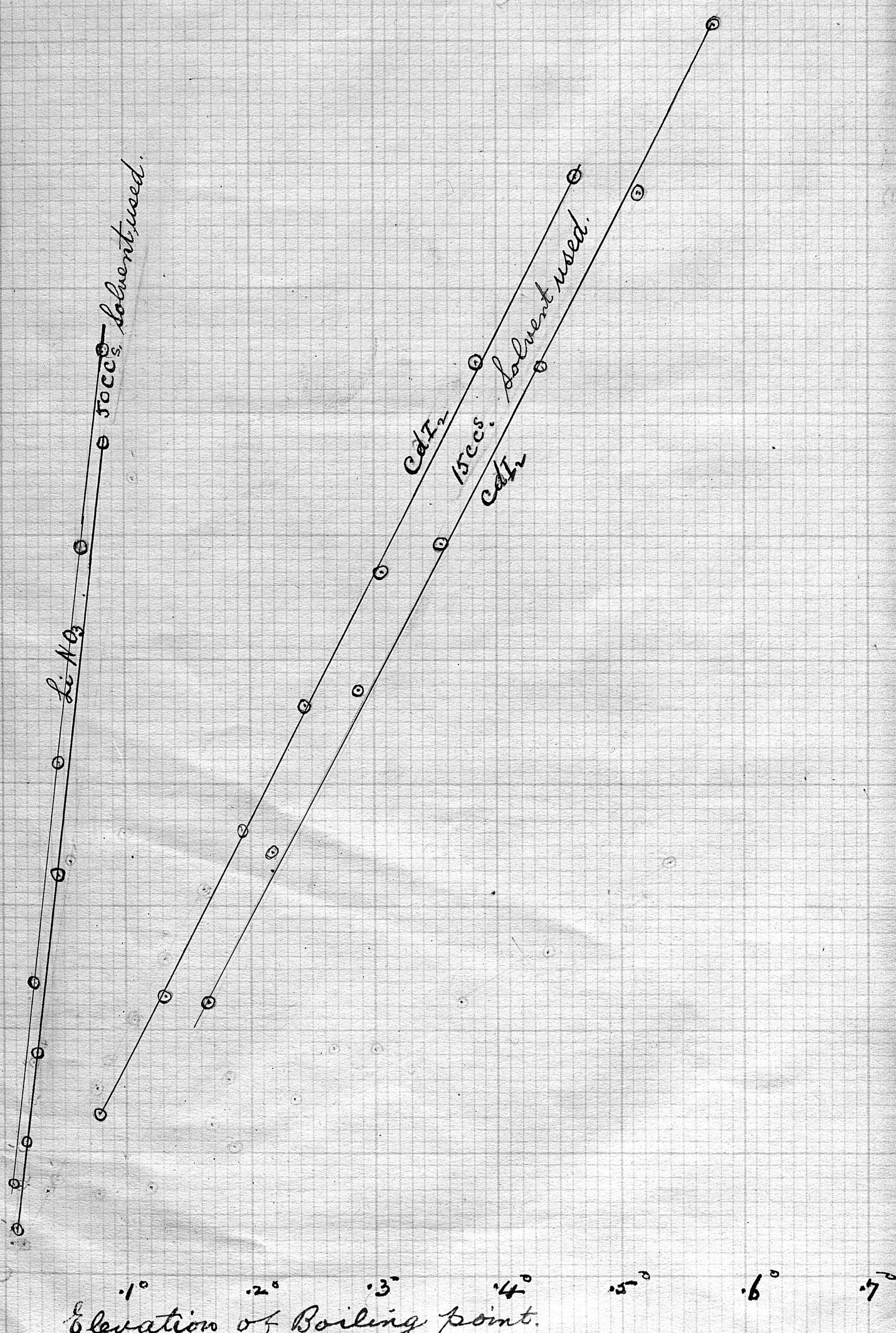
Elevation /

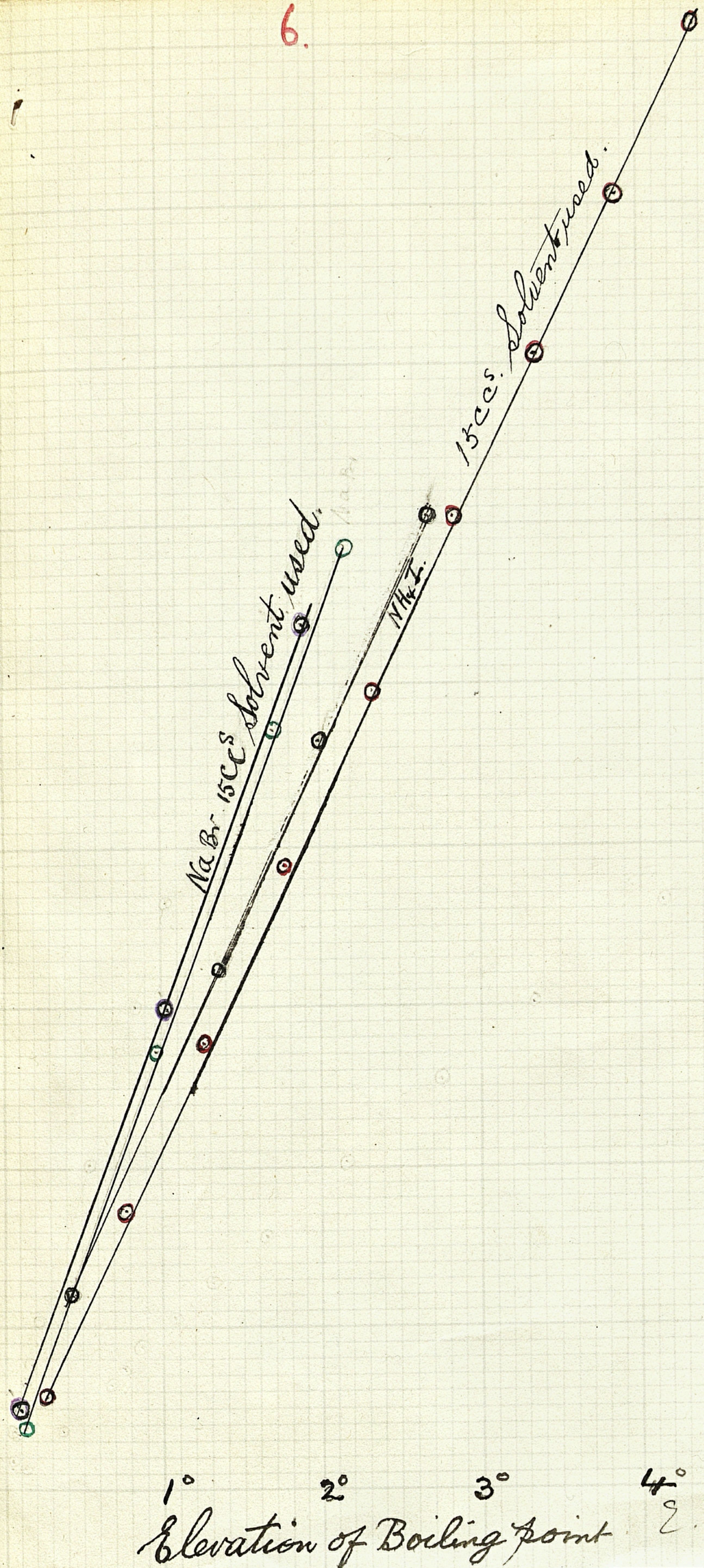
*Proc. Royal Society Vol. XXV part 11 page 956. (Paper herewith).
** " " " " " " " 955.
***"Zeit für Phys. Chem, 40 - 185. "(1902)
*1 Zeit. für Phys. Chem, 40 - 185. (1902)
*2 " " " " " " "

Elevation of boiling point weight of salt added curves are given (pages 5-6) for Na Br, NH_4I, Li No_3 and Cd I_2. which illustrate the parallelism and straightness which have been pointed out.*

When comparing curves for different salts the scale on which they are drawn should be noted.

* Proc. Royal Society £.25, (11) 956. (1905). (Paper herewith pp 5-6).


Cal I₂
15 ccs. Solvent used.
Cal I₂
15 ccs. Solvent used.
Cal I₂
15 ccs. Solvent used.


Na Br. 15cc.s Solvent used.
NH4I.
15cc.s. Solvent used.
1°
2°
3°
4°
Elevation of Boiling point

Part (2).

Conductivity Measurements.

An improved method of obtaining these at high temperatures.

To obtain the results which will be given in parts (3) and (4) of this paper, it was imperative to obtain conductivity values for a large variation of concentration at or near the boiling point of the solvent. In consequence of these being required at so high a temperature, and at the concentrations which I shall afterwards require practically no available data were obtainable. A multiplicity of conductivity determinations have been made at temperatures up to 80° centigrade, but this would be too low a temperature for my purpose. *Kraunhals to whom I was indebted for data at 99.4° centigrade in part 1 of this paper does not give conductivity values at any concentration for the salts under consideration in parts (3) and (4) except Potassium Bromide, and these only for dilute solutions. I have also to express indebtedness to[1] Lyle and Hosking for conductivity values used in the case of Na cl solutions.

In all other instances the conductivity values are my own.

To obtain these I designed two Electrolytic cells suitable for direct heating, one for dilute, the other for concentrated solutions. Photographs are given also a rough sketch of each, Figs[xx] (1) and (2). Fig (1) represents a section of the tube for dilute solutions, with a range say, from normal to one or two thousandths normal. B. is the outer or boiling tube, the tube D. contains when the apparatus is in use, a condensing tube of the Beckmann pattern. C. is an inner tube fitted into B. by means of a rubber stopper F. through a hole which it fits tightly. The electrodes E. and the thermometer T. reading to tenths from 97°-100° centigrade, and having its scale entirely

above /

* Zeit. für. Phys. Chemic 5, 250. (1890)
1 Phil. Mag. (6) 3, 487. (1902)
xx Pages 12, 13 of this paper.

above ~~B.B.~~ b b' Both are placed in the inner tube C. which is perforated at a and a^1, the one opening allowing the solution placed in the boiling tube B. to pass into or out of the inner tube, the other allowing the vapour formed in C. to pass over to the condensing tube D. The glass tubes b. and b^1. leading to the electrodes, and making mercurial contact with platinum wires passing into these, and to the electrodes as represented in the figure, pass through a vulcanite top $b.b^1$ in which they are cemented, and through a rubber stopper into the inner tube, the thermometer does so also but is not sealed into the vulcanite top. The wires to the bridge as represented in the figure pass into the mercury in the electrode tubes, and make connection with the bridge. A little side tube G. was attached and fitted with a rubber stopper in case more concentrated solutions by the addition of salt were required.

The tube designed for strong solutions with which conductivities may be measured from half normal solutions to any degree of normality desired is represented in Fig. (2) A.Al is the boiling tube, which has two limbs, with short tubes, D and D^1 attached to hold a small condenser of the Beckmann pattern. The tubes have each a short resistance portion, as represented, E and E^1 are the electrodes not fitting tightly the tubes in which they are placed. The glass connection tubes F and F^1 pass through rubber stoppers C and C^1 and the vulcanite tops A and A^1 into which they are adjustably fixed by means of a screw arrangement at B. The screw is so constructed as to press against a little cushion of rubber which presses against the glass tube and may be made to do so as firmly as desired. The wires to the bridge are as in the tube for dilute solutions already described.

The resistance tubes were all made of Jena glass, that is the boiling tube, the inner one, and those making mercurial connection to the electrodes which were of thick platinum foil.

In conductivity work the purest water is essential. This was obtained by using distilled water which was redistilled from a flask containing a little Potassium bichromate in acid solution into one containing /

containing a small quantity of Barium Hydrate, thence to a condenser and Jena glass flask for its reception.

To preserve the purity of the water it was kept in a Jena glass bottle. By the method above described for water purification a purity was reached of ·21 x 10^{-6} Kohlrausche units Cm^{-1} Ohm^{-1}. During the time the experiments were being made the results of which are given a register of water purity was kept which shows that from this standard there was only slight divergence.

In conductivity work a wheatstone bridge after the Kohlrausche pattern for electrolytes and telephone were used. The bridge was carefully calibrated and the electrodes of the resistance tubes were platinised by the Kohlrausche method. Observations were made to determine the amount of vapour present in the tube during an experiment which was allowed for. It was assumed that in finding values of $\frac{Mv}{1000D}$ for the boiling point, the ratio of the dilutions at 100° Centigrade might be taken equal to the corresponding ratio at 15°.

The solutions were made up at 15° centigrade by the aid of a Thermostat and were of known concentration. In making up these a table of solubilities was consulted and the highest concentration in harmony selected. Five hundred or a thousand C.cs. of solution were made up at this concentration. This was done by weighing so many gramme equivalents of salt according to the concentration desired placing it in a flask, dissolving in water and bringing the solution to the standard volume 500 or 1000 C.cs at 15°.

The various dilutions were obtained from this by the addition of solvent to a measured number of C,cs. of solution. For this 20, 25, and 50 C.cs. pipettes were used and 100, 200, 300 and 500 C.C. flasks. One of these dilutions, usually the tenth normal was tested quantitatively as a safeguard against error. As it was obtained from the most concentrated solution its accuracy was proof of that of both. The method adopted gave every satisfaction, the results being obtained easily without any undue waste of time.

The /

The duplications at normal or half normal and at ∞ indicate an error limit for the former of one half per cent, and the latter of two and one half per cent.

The results are given in tables and graphically from several standpoints.

For my purpose μ_V was all that was necessary but I also give the conductivity values, Ionization has been plotted (1st) against gramme equivalents per litre; (2nd) against grams of salt added to a constant amount of solvent, and (3rd) against per centage composition. If these be spoken of as curves 1, 2, and 3, it will be seen that the curves number (2) are very much straighter than curves (1) and that those of (3) are still straighter. These results are interesting from the standpoint of reading values from curves*.

I have also plotted conductivity against the number of litres to the gramme equivalent.

It will be noted that I have found conductivity values at very high concentration, indeed in some cases beyond the solubility at 15° centigrade. These were obtained for a reason which will appear in part IV of this paper, as follows.

I desired the conductivity at a certain concentration beyond solubility at 15° but within the solubility at 100° centigrade. In each case, I calculated the amount of salt required to the amount of solvent to be used in the experiment, and placed it in the boiling resistance tube, adding the solvent afterwards. This was then heated to the desired temperature and the reading taken. Several such experiments were made on various salts, the results so obtained are marked with an asterisk. Duplicate readings were taken as a rule for the normal or half normal solution, one with each tube, the one thus acted as a check on the other. The duplicate values as a rule were approximately the same, in some instances they are in entire harmony. The conductivity value at two thousandth was sometimes almost the same as that at one thousandth /

* Dr Gibson has pointed out a somewhat similar result in a paper read recently at the Royal Society Edinburgh.

thousandth normal. In one or two instances it was considerably more The curves I have obtained correspond with those of other observers when their values are plotted but different salts have been used.

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Part I

An improvement in the method of determining Elevation.

Note on the Boiling Points of Aqueous Solutions.

By **Rev. S. M. Johnston**, B.A.

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Note on the Boiling Points of Aqueous Solutions.

By the Rev. S. M. Johnston, B.A. *Communicated by* Professor J. G. MacGregor, F.R.S.

(MS. received July 17, 1905. Read same date.)

In the course of a research on the boiling points of aqueous solutions, certain points came under my notice which have been introduced into this note.

After considerable experience with various forms of Beckmann's boiling point apparatus, and due consideration of the Jones type, a boiling point apparatus was designed which embraced what were considered the best points of each, in view of the research anticipated. The body of the tube was of the Jones type, and had a side tube fitted with a rubber stopper for the introduction of the salt at a short distance from the top of the tube. On the opposite side of the boiling tube, about the same height up, went off a condensing tube of the Beckmann pattern. The thermometer—one of Beckmann's—read to hundredths of a degree, and, with the aid of a Beckmann reading glass, could be estimated to thousandths of a degree. It passed through a close-fitting rubber stopper at the top of the tube.

In carrying out an experiment, garnets and platinum tetrahedra were used for filling material. The thermometer, when in position, was surrounded to a point above the surface of the solvent or solutions by a cylinder of platinum foil. Beneath the thermometer a few pieces of platinum foil were placed. The boiling tube was surrounded externally by a cylinder of glass of considerably larger diameter, and the space between was packed with asbestos wool. The heat was supplied by a gas jet, which was prevented from coming into contact with the boiling tube by wire gauze and asbestos paper. The whole apparatus was surrounded by a zinc cylinder in two portions, one of which could be removed at pleasure.

With these precautions, a steady boiling temperature could be

quickly obtained,—so steady that, notwithstanding the delicacy of the thermometer used, no change of reading could be detected frequently for five or ten minutes, and sometimes for longer periods.

In the experiments, the amount of solvent delivered by a fifty c.c. pipette was used. As the result of several experiments to determine the amount of vapour in the tube during an experiment, it was found to be ·41 grammes, and was allowed for. The distilled water used was redistilled to guard against impurities. The filling material, after each series of experiments, was thoroughly cleansed with boiling water and dried before being used again. The platinum foil, in addition, was heated in a Bunsen flame.

Series of solutions were made from each salt by the addition of compressed pellets of salt successively to the solvent or solution during ebullition. The pellets were made at first by the aid of a steel press, but later by one with ivory fittings, to safeguard their purity, which was essential when deliquescent salts were the subject of research.

The procedure adopted was to bring the solvent to a steady boiling temperature, which was noted. Then pellet after pellet of salt was added at intervals of from twenty to twenty-five minutes, the boiling temperature of the successive concentrations being noted. It was found essential to the success of an experiment to allow at least twenty minutes for the diffusion of the salt. Corresponding to the successive readings of the thermometer, a succession of readings of the barometer was taken, so that any change in atmospheric pressure might be allowed for. The barometer gave readings corresponding to four thousandths of a degree, but could be estimated to the equivalent of two thousandths.

The salts used were supplied by Messrs Merck & Co. as specially pure, and were tested quantitatively and spectroscopically.

In the calculation of results ionization coefficients were necessary at high temperature, as near the boiling point as possible. These were obtained from conductivity values as given by Kranhals * as follows. Kranhals gives the molecular conduc-

* *Zeit. für phys. Chem.*, 5, 250. 1890.

tivity at 99°·4 C. for solutions containing one, one-half, one-fourth, one-eighth, etc. and one-thousandth gramme equivalents per litre. The ionization at any of these concentrations was obtained by dividing the conductivity value, as given by Kranhals, by the value at one-thousandth gramme equivalents. The concentration ionization curve was drawn on sectional paper for the range of a series of experiments. From the amount of salt added to the solvent the percentage composition was obtained, from which, by the aid of tables,* the concentration in equivalent gramme molecules per litre was obtained, and for this the ionization by the use of the ionization concentration curve already referred to. Kranhals claims to work with an error limit of from two to three per cent. Having repeated many of his experiments, I found this claim well justified. Schaller, and Lyle and Hosking have also done some conductivity work at 99° or 99°·4. Kranhals' values were chosen because they were best suited to series of experiments within the range of this note. Lyle and Hosking † deal chiefly with sodium chloride solutions. Schaller ‡ worked principally at 256, 512, and 1024 litres per gramme equivalent. Values up to 80° have been given by Trötsch,§ and Campetti and Nazari,‖ which would be too low a temperature for my purpose. Those who have given conductivity values up to 99° or 99°·4 have only given them to about one-thousandth gramme equivalents per litre, which dilution could scarcely be supposed to give the molecular conductivity at infinite dilution for every salt.

I therefore intend to make determinations of conductivity at greater dilution.

When calculating the results obtained by experiment, *at first*, total elevations above the boiling point of the solvent were used. The calculations were made from the formula

$$C = \frac{m.W.E}{(1+n-1\alpha)w},$$

where C is the value of the so-called boiling point elevation

* *B. A. Report on the Present State of our Knowledge of Electrolysis and Electro-Chemistry*, 1893.

† *Phil. Mag.* (6), 3, 487. 1902.

‡ *Zeit. f. phys. Chem.*, 25, 497.

§ *Wied. Annalen*, 41, 259. 1890.

‖ *Acad. Science Torino*, 40, Nos. 2 and 3, pp. 155, 163. 1904–5.

constant expressed per gramme particle (molecule or ion) in one gramme of solvent—

m = molecular weight of salt added.

W = weight of solvent used in grammes.

E = elevation of boiling point.

w = weight of salt added in grammes.

α = ionization coefficient.

n = number of free ions into which a molecule of salt dissociates.

From this formula values of C were obtained, at one time high, at another low, when compared with theory. Thus, for potassium chloride the values 858, 704, 684, 643, 614, 596, 572 were obtained from one series; a second series gave 460, 467, 514, 518, 523. For potassium nitrate the values were 637, 617, 603, 573, 571, 549, 547, 540, and a second series gave 874, 702, 696, 686, 643, 608, 609, 593; for a third series the values were 605, 556, 550. For sodium nitrate 518, 516, 520, 529, 534, 530, 535. For sodium chloride 617, 621, 592, 587, 579.

Such values as these being obtained, it was desirable to see what values would be given by calculations from the boiling point data of other experimenters. Elevations of boiling point as given by Biltz * gave for potassium nitrate as values 638, 589, 596, 628, and for sodium chloride 585, 598, 611, 609. Those given by Walker and Lumsden † gave for potassium nitrate 648, 618, for sodium chloride 598, 593, and for potassium bromide 620, 614, 645, 665. Smitz's ‡ elevations gave for sodium chloride 463, for potassium chloride 497, for potassium nitrate 522, and for sodium nitrate 594.

From observations I made, it would seem that these high values are the result of a difficulty in the determination of the exact boiling point of water. Thus, for the solvent, a steady boiling temperature could be raised or lowered by increasing or decreasing the strength of the source of heat, within the range of several hundredths of a degree. A solution, on the other hand, took up a definite boiling temperature, which was independent of small changes in the strength of the source of heat so long as ebullition was maintained.

* *Practical Methods for determining Molecular Weights*, translated by Jones and King, 189. 1899.

† *Journal of the Chemical Society*, **73**, 502. 1898.

‡ *Zeitschrift für physicalische Chemie*, 39, 420. 1902.

Several series of experiments were performed on each of a number of salts to find the relation between the boiling point elevation of different series on the same salt. It was seen from plotting elevations of boiling temperature against weight of salt added, and drawing in the curves for different series on the same salt, that the curves obtained were approximately straight lines, and parallel to each other. Specimens of these are given for potassium nitrate, barium chloride, and lithium chloride on page 957; ammonium sulphate and potassium chloride on page 958; and sodium nitrate on page 959. The straightness of the curves in the vicinity of the origin was also tested in some cases, and it was found that, so far as experiment could be carried, the curves continued approximately straight lines.

The boiling temperature of the solvent under these considerations being looked upon as at fault, that is, its experimental value varying by one or two hundredths of a degree, and the boiling temperature of a solution being steady, it became desirable, in determining the boiling point constant, to use only elevations above the boiling point of a solution. I consequently computed, not the elevation of the boiling point per gramme particle produced by adding a given number of grammes of salt to one gramme of solvent, but the elevation per gramme particle produced by adding given numbers of gramme molecules of salt to a solution, the expression employed being

$$C = \frac{m.W.\Delta E}{(1 + n - 1\alpha)\Delta w},$$

where m, W, n and α are as before, and ΔE and Δw increments of elevation of boiling temperature and grammes of salt added respectively. According to theory, the values obtained should be the same as those from the first formula if the E could be accurately determined. The ratio $\frac{\Delta E}{\Delta w}$ was found as follows:—

Let OW and OE be axes of weight of salt added and elevation of boiling temperature respectively. Let LR, the curve for any series of observations, found as seen above to be approximately a straight line, be produced to meet the axes in P. Through any near points Q and R on this curve draw parallels to the axes.

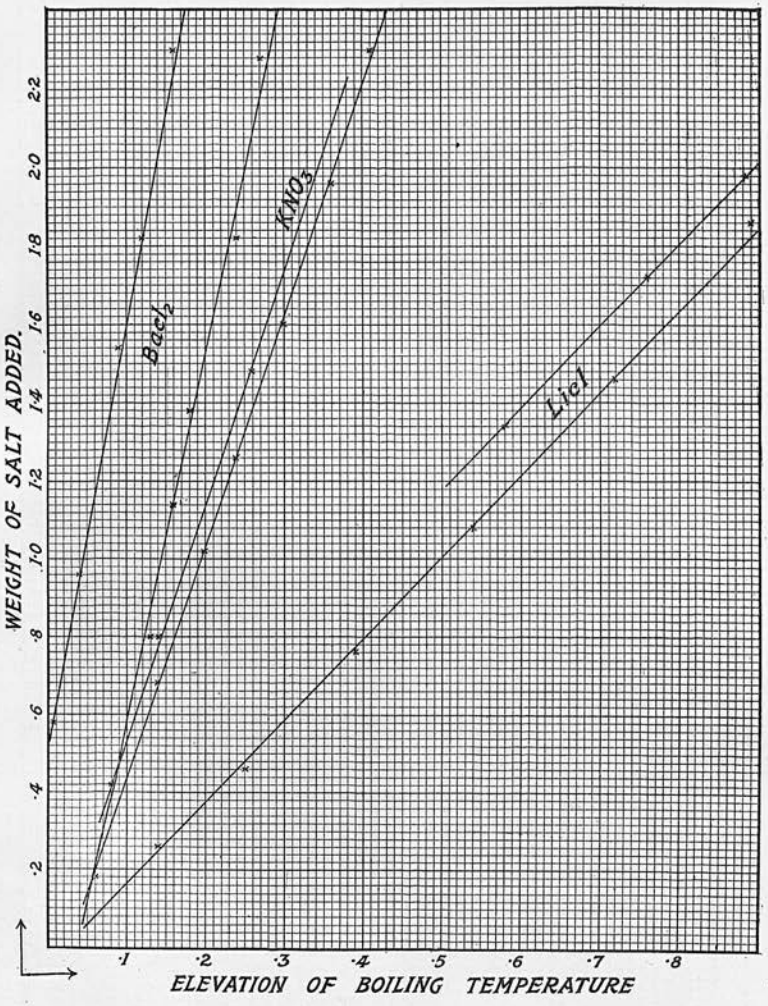

WEIGHT OF SALT ADDED.
·2
·4
·6
·8
1·0
1·2
1·4
1·6
1·8
2·0
2·2
BaCl2
KNO3
LiCl
·1
·2
·3
·4
·5
·6
·7
·8
ELEVATION OF BOILING TEMPERATURE

FIG. 1.

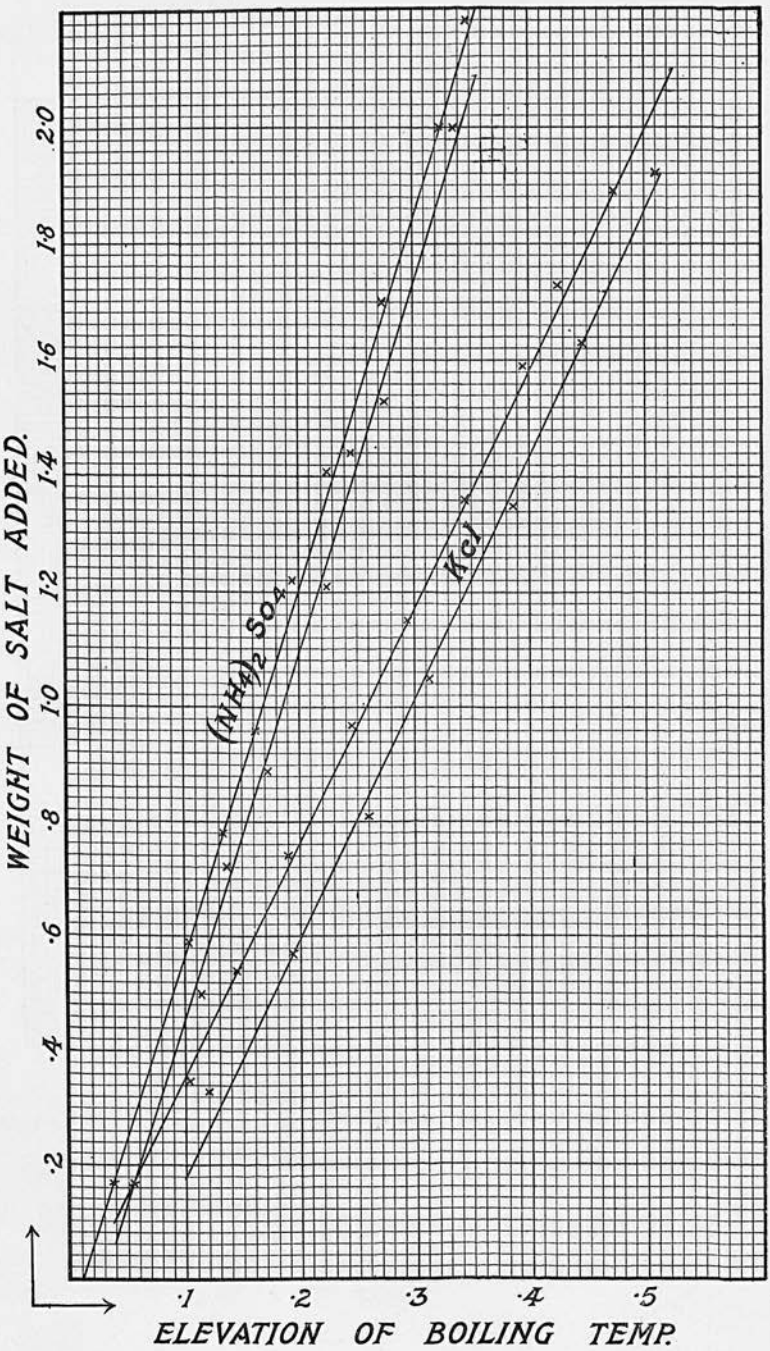

WEIGHT OF SALT ADDED.
·2
·4
·6
·8
1·0
1·2
1·4
1·6
1·8
2·0
(NH4)2 SO4
KCl
·1
·2
·3
·4
·5
ELEVATION OF BOILING TEMP.

FIG. 2.

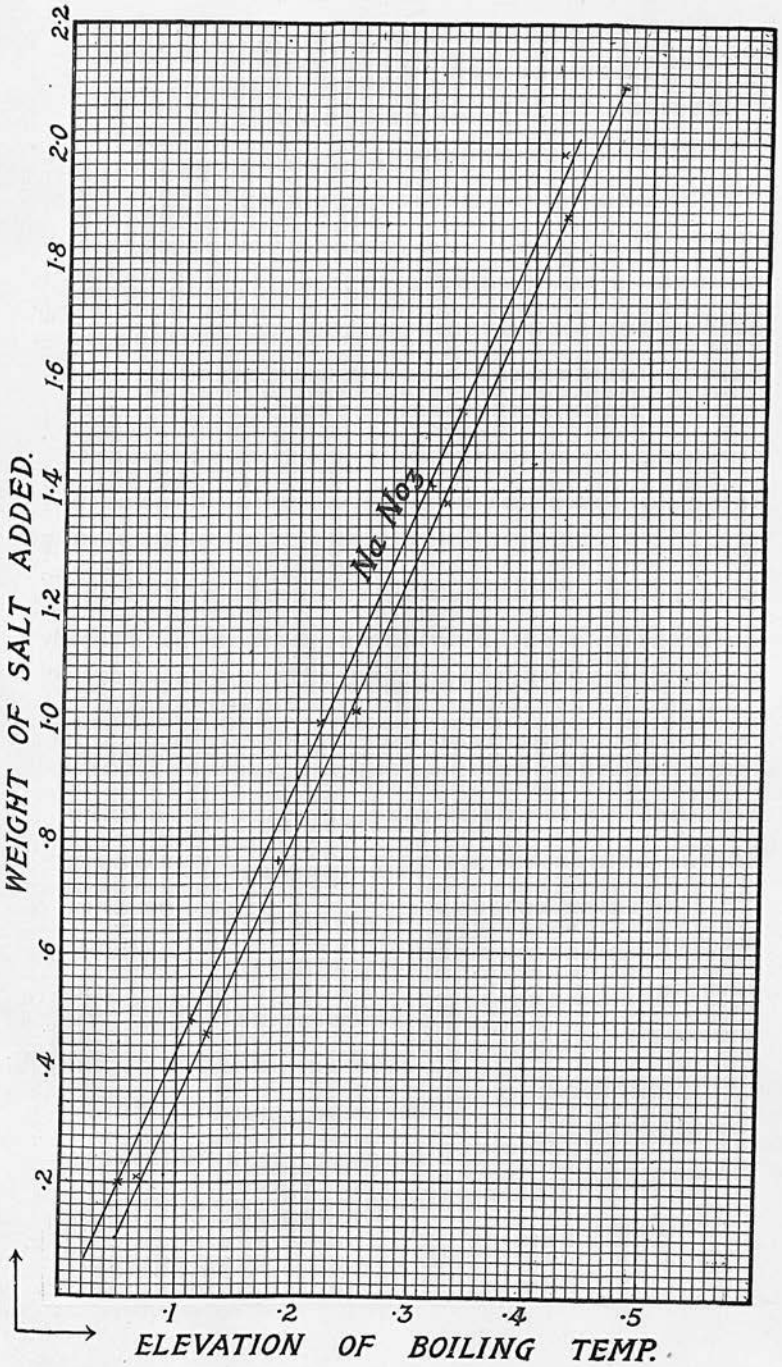

WEIGHT OF SALT ADDED.
·2
·4
·6
·8
1·0
1·2
1·4
1·6
1·8
2·0
2·2
NaNO3
·1
·2
·3
·4
·5
ELEVATION OF BOILING TEMP.

FIG. 3.

$$\frac{\Delta E}{\Delta w} = \frac{QS}{RS}$$

$$= \frac{PT}{TR}$$

$$= \frac{OT - OP}{TR}$$

$$= \frac{E - OP}{w}.$$

Hence $C = \frac{E - OP}{w}\left(\frac{mW}{1 + n - 1\alpha}\right)$.

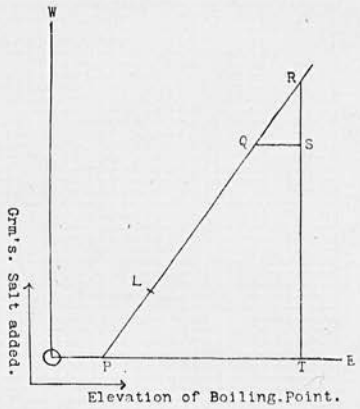


FIG. 4.

Values of $\frac{\Delta E}{\Delta w}$ were obtained from those of E and w by reading off OP and deducting it from the observed value of E and dividing by w. The following tables contain the results of the determination of C. As Kranhals only claims an accuracy in his conductivity data of two to three per cent., I have usually considered it sufficient to calculate ionizations to two places of decimals. In the case of sodium nitrate the elevations of boiling temperature used were the observed values, but for the other salts the elevation values were taken from the curves.

POTASSIUM NITRATE.

First Series.

Grms. Salt added.	Per cent. Composition.	Grm. eqs. per Litre.	Elevation of Boiling Point.	Ionization Co-eff.	Elev. Constant.
·2118	·42	·041	·063	·665	519
·445	·89	·089	·112	·657	511
·6986	1·39	·139	·160	·642	514
·9318	1·85	·187	·206	·629	521
1·2126	2·39	·244	·252	·616	518
1·5044	2·95	·301	·292	·611	516
1·8366	3·57	·364	·348	·608	516
2·1876	4·23	·431	·403	·605	516

Second Series.

·4300	·86	·086	·086	·657	512
·8120	1·61	·162	·149	·635	512
1·493	2·92	·298	·265	·611	516

Potassium Chloride.

First Series.

Grms. Salt added.	Per cent. Composition.	Grm. eqs. per Litre.	Elevation of Boiling Point.	Ionization. Co-eff.	Elev. Constant.
·1754	·35	·048	·054	·89	527
·3546	·71	·124	·101	·88	521
·5424	1·08	·144	·146	·87	503
·7426	1·47	·202	·190	·85	500
·9740	1·93	·266	·247	·83	500
1·1520	2·26	·316	·291	·81	505
1·3684	2·69	·370	·343	·79	504
1·592a	3·11	·428	·394	·77	511
1·7278	3·37	·466	·425	·76	512
1·8918	3·68	·508	·471	·75	517

Second Series.

·1975	·39	·050	·058	·89	522
·3164	·63	·084	·078	·88	502
·5386	1·07	·146	·129	·87	501
·6736	1·34	·164	·171	·85	495
·8236	1·63	·224	·216	·84	497
1·0228	2·02	·298	·258	·81	497
1·1742	2·31	·318	·297	·81	502
1·2970	2·55	·356	·329	·80	503
1·5382	3·01	·414	·372	·78	508
1·7364	3·39	·468	·421	·76	512
1·9388	3·77	·516	·489	·74	523
2·1434	4·15	·570	·535	·73	525

Third Series.

·3300	·66	·090	·120	·88	503
·5500	1·09	·248	·191	·87	509
·8084	1·60	·230	·260	·84	510
1·0460	2·07	·288	·312	·81	516
1·3558	2·66	·366	·388	·79	518
1·6300	3·19	·440	·444	·76	520
1·9224	3·74	·512	·510	·74	521
2·2144	4·28	·590	·582	·72	529
2·5328	4·87	·674	·666	·71	530

Sodium Nitrate.

First Series.

Grms. Salt added.	Per cent. Composition.	Grm. eqs. per Litre.	Elevation of Boiling Point.	Ionization.	Elev. Constant.
·2054	·36	·042	·053	·87	500
·4860	·87	·105	·111	·82	500
1·0198	1·81	·218	·220	·76	500
1·4880	2·50	·302	·312	·70	505
1·9852	3·60	·435	·420	·65	530
2·5216	4·80	·578	·530	·62	536
3·0242	5·54	·667	·632	·59	540
3·5682	6·58	·744	·700	·54	531

Second Series.

·2156	·37	·046	·066	·87	499
·4625	·82	·101	·125	·82	517
·7628	1·43	·173	·186	·78	517
1·0879	2·04	·247	·262	·76	525
1·3831	2·64	·319	·316	·70	530
1·5883	3·02	·367	·359	·67	536
1·8682	3·56	·431	·428	·65	550
2·2619	4·32	·521	·509	·63	552

Potassium Bromide.

First Series.

Grms. Salt added.	Per cent. Composition.	Grm. eqs. per Litre.	Elevation of Boiling Point.	Ionization Co-eff.	Elev. Constant.
·4250	·85	·088	·112	·796	504
·6854	1·36	·140	·161	·774	502
·8813	1·75	·170	·198	·758	509
1·0293	2·03	·208	·223	·744	519
1·2945	2·55	·260	·252	·732	520
1·5705	3·07	·312	·312	·720	525
1·9564	3·88	·396	·374	·706	528
2·3074	4·45	·456	·435	·692	535

Second Series.

Grms. Salt added.	Per cent. Composition.	Grm. eqs. per Litre.	Elevation of Boiling Point.	Ionization Co-eff.	Elev. Constant.
·5530	1·14	·116	·078	·786	520
·8060	1·60	·168	·105	·764	515
1·0248	2·02	·208	·131	·744	519
1·1754	2·32	·332	·157	·734	521
2·2978	4·44	·456	·342	·694	530
2·5470	4·88	·500	·379	·688	531
2·8726	5·48	·592	·428	·676	535
3·2479	6·16	·632	·483	·660	536
3·4952	6·60	·680	·529	·652	537

SODIUM CHLORIDE.

First Series.

Grms. Salt added.	Per cent. Composition.	Grm. eqs. per Litre.	Elevation of Boiling Point.	Ionization Co-eff.	Elev. Constant.
·2070	·48	·080	·096	·79	503
·4294	·91	·162	·169	·76	518
·6143	1·23	·218	·228	·71	522
·8314	1·66	·294	·294	·68	523
1·0277	2·01	·354	·356	·67	525
1·2160	2·38	·404	·421	·66	523
1·5870	2·98	·528	·541	·65	526
2·0284	3·88	·634	·680	·65	525
2·5044	4·80	·856	·826	·64	524
2·9744	5·68	1·004	·986	·64	525
3·4182	6·47	1·148	1·144	·63	525

Second Series.

·2384	·483	·082	·136	·79	509
·4018	·80	·140	·179	·76	518
·6852	1·36	·242	·285	·71	518
·8862	1·76	·312	·347	·68	522
1·1136	2·06	·356	·499	·67	526
1·3978	2·74	·486	·494	·66	527
1·7802	3·47	·614	·610	·65	526
2·1962	4·25	·752	·715	·65	521
2·6150	5·02	·892	·821	·64	525
2·9736	5·67	1·008	·929	·64	527
3·2832	6·22	1·102	1·013	·64	525

If the values *just given* for C be compared with those obtained when elevations above the boiling point of the solvent were used, as in the calculations on page 955, it will be obvious they are in much greater harmony for the same series. It will also be seen that the values of C for one series, when compared with those for another on the same salt, are in greater harmony; and the increased agreement is maintained when the values for series on different salts are considered. The agreement of the values with theory is also much greater.

Most of the values obtained for C indicate an increase of the value with increase of concentration; but it would be premature to draw that inference, as in solutions so dilute as some of those used, a small ionization error would cause a considerable variation; but in addition it has to be remembered that for some of the dilutions used, one-thousandth of a degree variation of boiling temperature would have made a difference of 10 in the value of C, and for any of the concentrations a few thousandths of a degree would have made a considerable change. It has also to be borne in mind that the barometer used, although an excellent instrument, only read to the equivalent of about four thousandths of a degree, and was estimated only to two thousandths. The first five values obtained for sodium nitrate in the first series are very approximately the same: during the time this series of observations was taken, no barometric change was detected. For potassium bromide the barometer remained steady for the last three experiments of the second series; and here, again, there is closer agreement than usual in the values of C. Also for the first series on potassium nitrate the barometer was steady, except in one observation, and here likewise the harmony of the values is increased. It would therefore seem probable that barometric changes, even after eliminating their effects by the ordinary method, have had considerable influence in producing variations in the value of C; consequently, were these deducted, the changes of value would be proportionately diminished. This is a source of error which it will be possible more fully to eliminate in later experiments.

The advantages of the method adopted become more apparent when it is applied to find molecular weights.

From the expression for C given above, page 956, we have

$$m = \frac{C.w.(1 + \overline{n - 1}\alpha)}{W(E - OP)}.$$

To illustrate this application of the method, I calculated the values of m for the bromide, chloride, and nitrate of potassium, and for sodium nitrate. The *first series*, as given above, in each was taken.

In the calculations the theoretical value of C, *i.e.* 520, was used. The values of m for potassium bromide were 121, 123, 120, 118, 118, 116, 115, 114: the mean value being 118·1, the recognised value 118·7. For potassium chloride the molecular values were 73, 73·3, 76, 76, 76, 76, 76, 74, 74, 74: their mean value is 74·83, the recognised value 74·59. For potassium nitrate the values were 101, 104, 102, 99·4, 100, 103, 103, 101; mean value, 101·2; recognised value, 101·17. For sodium nitrate the values were 86, 87, 87, 86, 85, 82, 80, 83, the arithmetic mean being 84·4, and the recognised value 85·08.

Had my object been the determination of molecular weights, greater care would have been taken when drawing the curves. The molecular weight calculations I have made indicate how accurately my method might be employed in such observations.

Up to the present the boiling-point method has only been applied roughly to determine molecular weights, and generally* with considerable divergence of value. This divergence would frequently have been much greater had not one error helped to counterbalance another. An inaccurate determination, usually too low, of the boiling point of the solvent when water was used, resulting in too high elevation of the boiling temperature of the solution, was largely overcome by the assumption of total ionization when the latter was only from seventy to ninety per cent. The variation is accentuated when molecular weights obtained by

* *Ber. Der. Chem.*, 31, 471. 1898.
Practical Methods for determining Molecular Weights, by . . . . Biltz, translated by Jones and King, p. 189. 1899.
Zeitschrift für Anorg. Chemie, 17, pp. 435 and 450. 1898.
Sakurai, *Journal of the Chemical Society*, 61, 987.
Walker and Lumsden, *Journal of the Chemical Society*, 73, 509. 1898.

different experimenters are considered, these varying for the same concentration by as much as twenty per cent.

It will thus be seen that molecular weight determinations by the boiling point method have been set on a much more satisfactory basis, and at the same time one giving better results. It is claimed, therefore, for the method adopted—namely, the determination of elevation per gramme equivalent by adding salt to a solution rather than to the solvent—that it gives to boiling point work on aqueous solutions greatly increased accuracy, whether we view it from the standpoint of values obtained for C, or from that of molecular weight determinations.

It may also be noted that as the manner in which the ionization coefficients were obtained and the formula used in calculating values of C were based, each on the dissociation theory, consequently the theory has been put to a somewhat severe test; and as the results agree so fully with theory, it has been entirely favourable.

The research was carried out at the Physical Laboratory of the Edinburgh University, and is to be continued.

(*Issued separately November* 4, 1905.

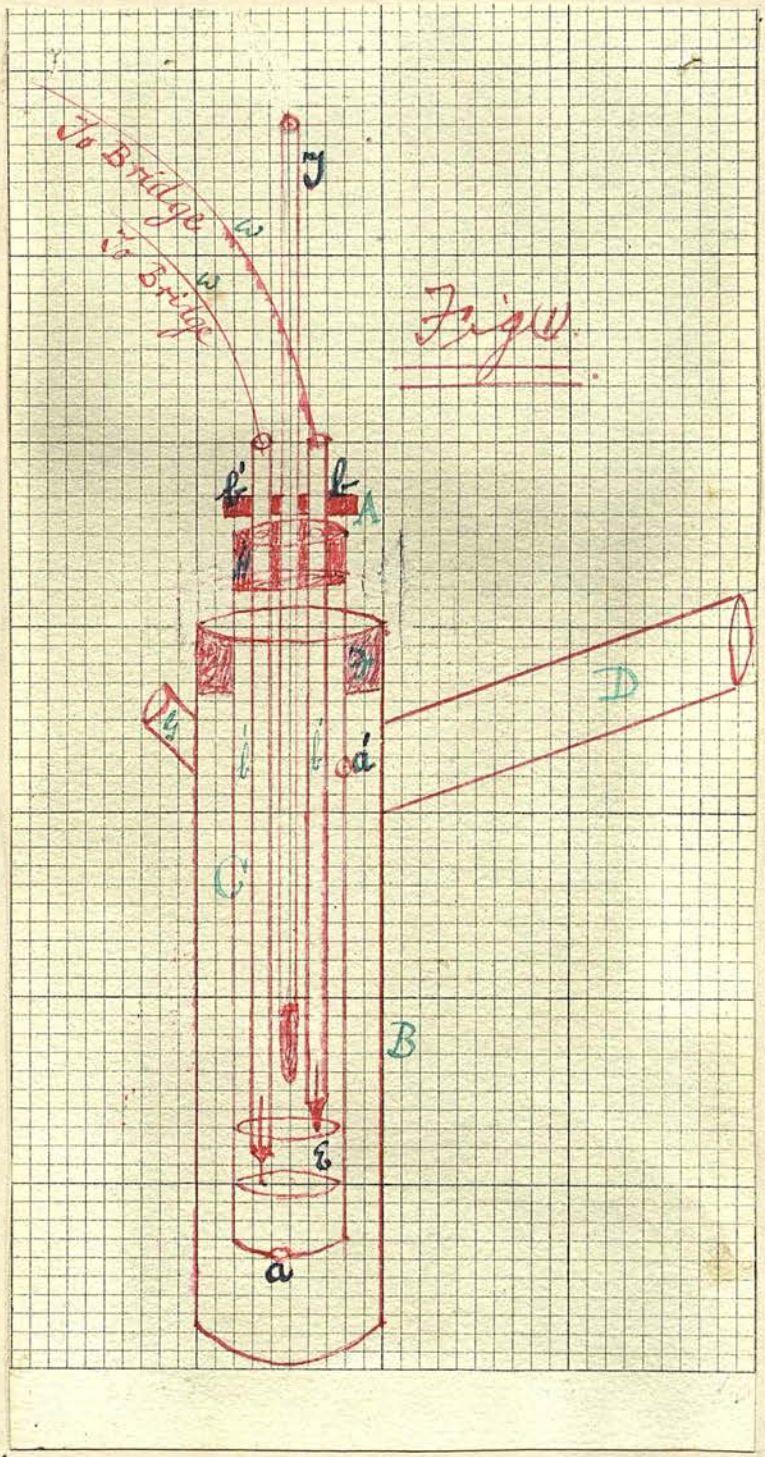


Fig. (1)

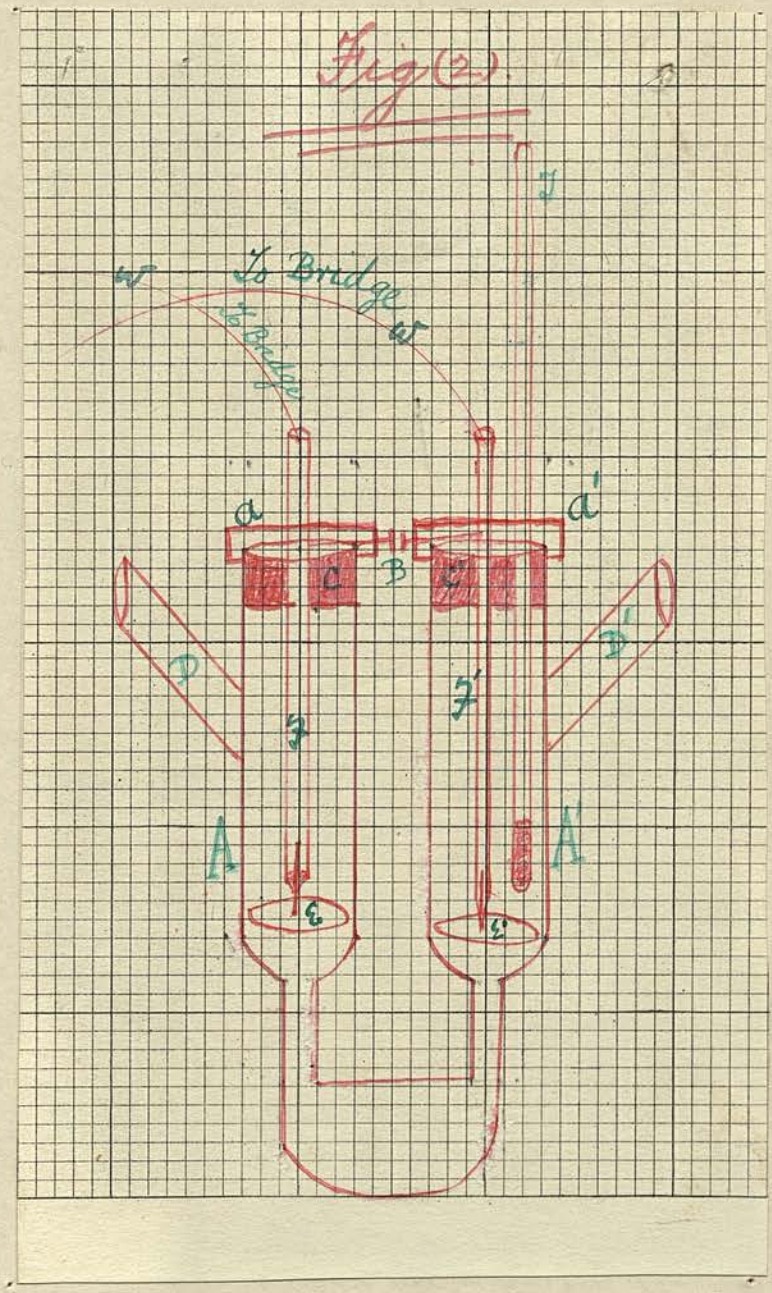
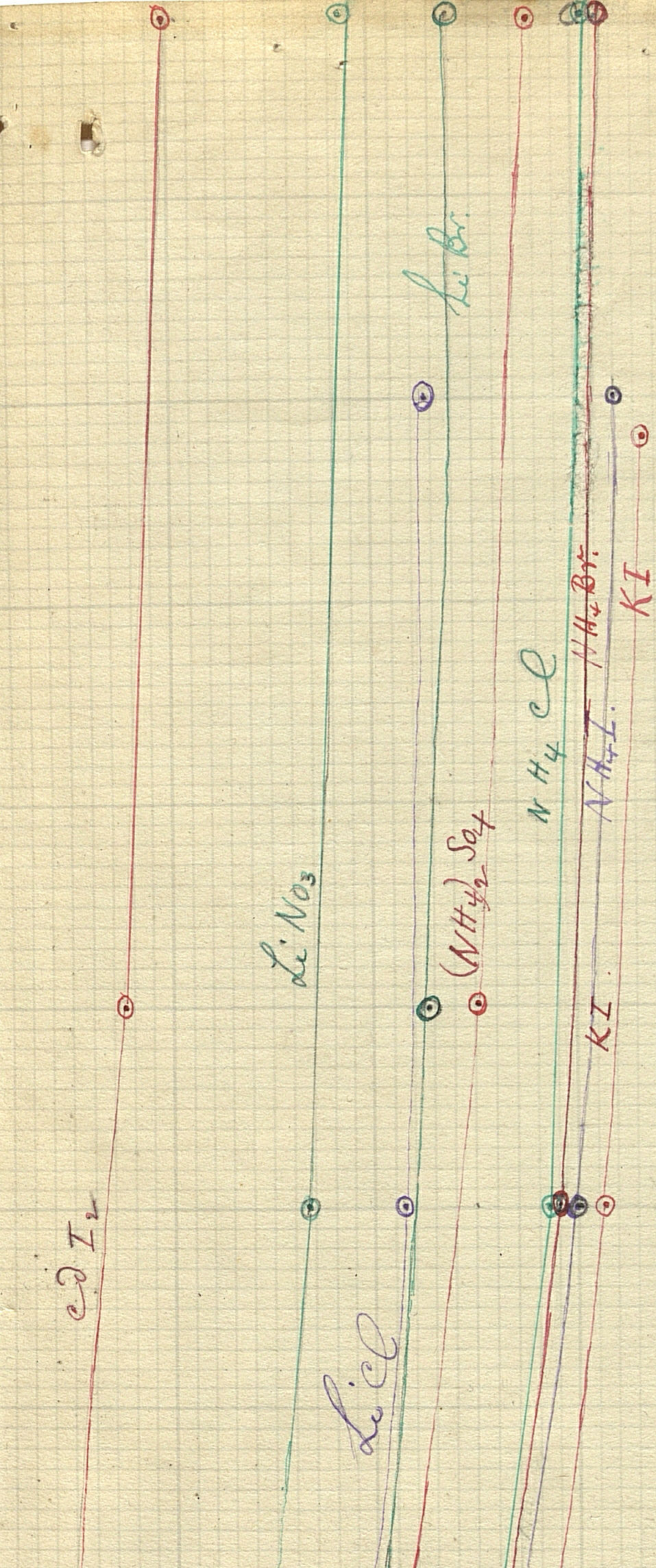


Fig. (2)

14.

X



Plotted from my own experiments, experimental values being used.

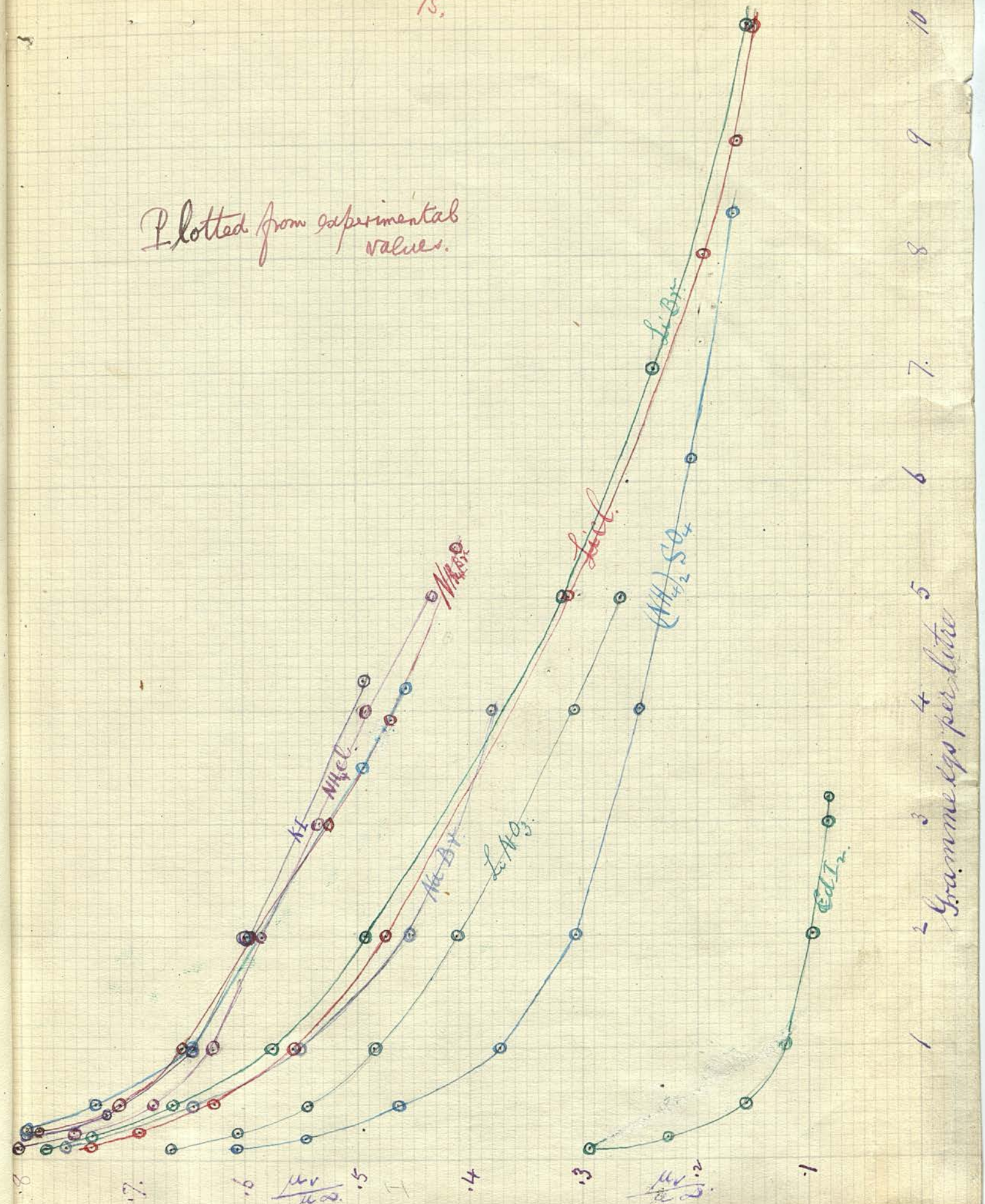
These curves are plotted from values given by Kranhals.

When they are compared with the corresponding curves I have plotted from my own values, their general characteristics are the same.

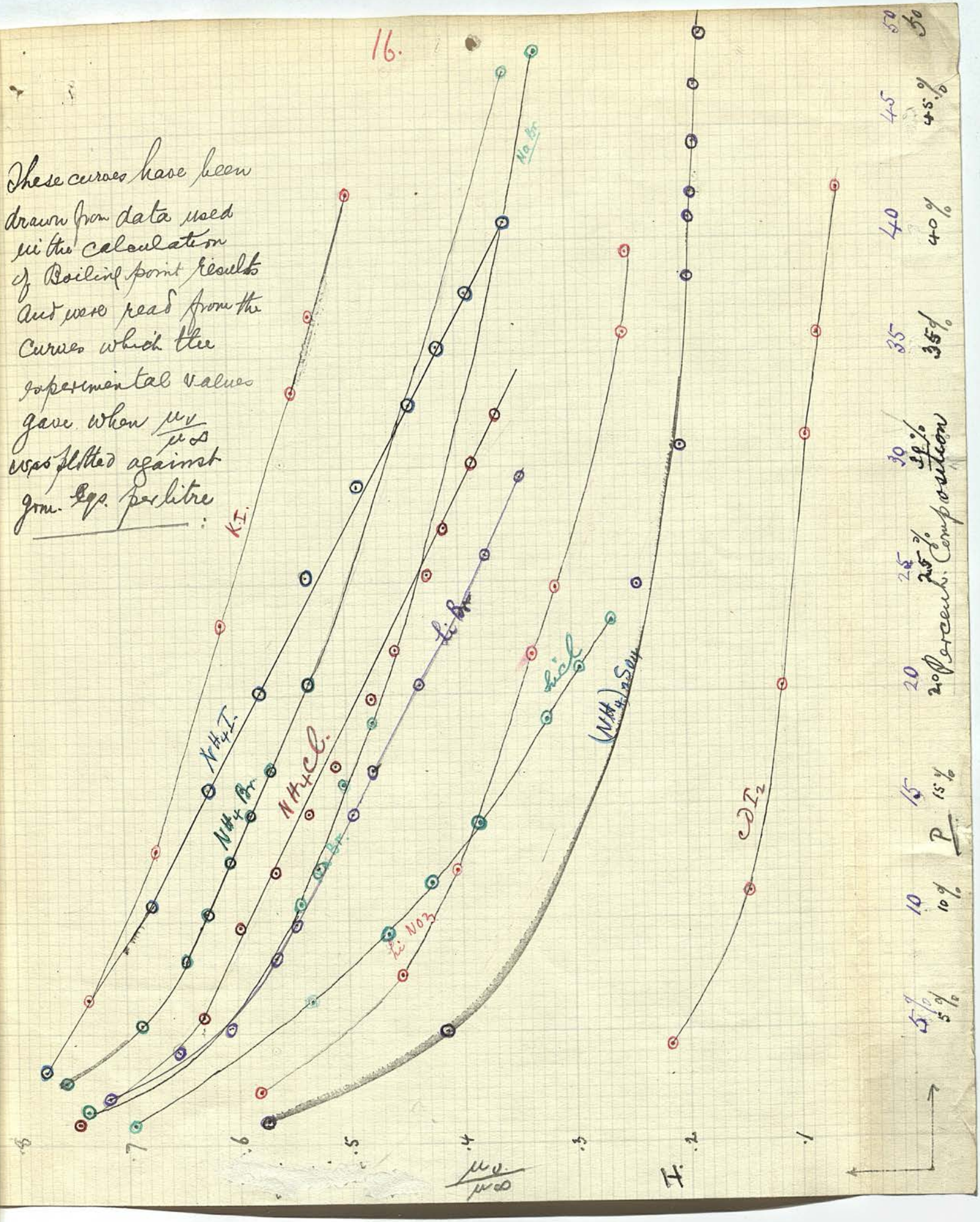
These are the only curves which have been plotted from values not obtained by myself.

1000 2000 3000

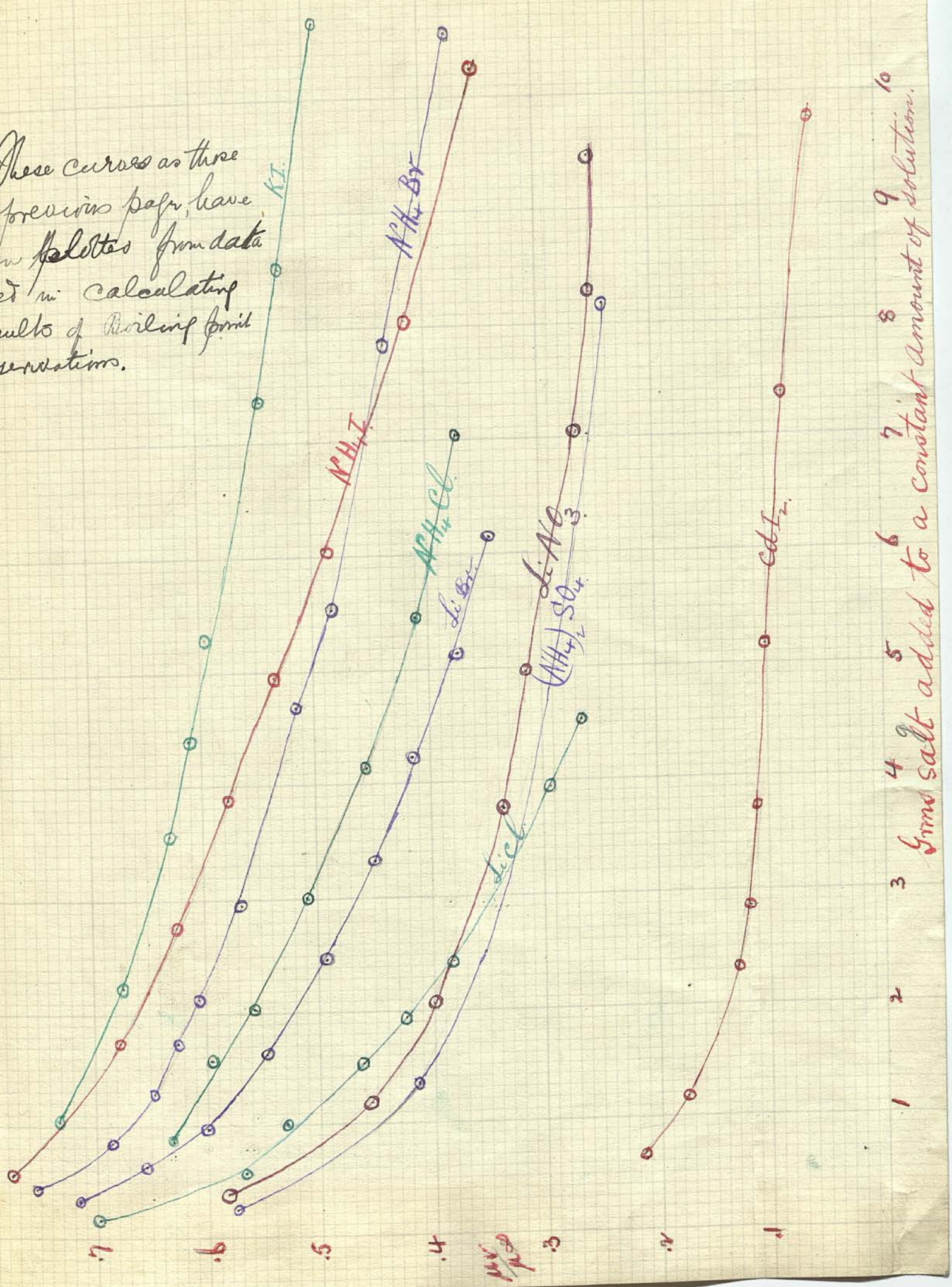
Plotted from experimental values.



These curves have been drawn from data used in the calculation of Boiling point results and were read from the curves which the experimental values gave when $\frac{\mu_v}{\mu_\infty}$ was plotted against grm. Eqs. per litre.



These curves as those in previous paper, have been plotted from data used in calculating results of Boiling point observations.



Ammonium Chloride.

Dilution Litres per Grm. Eq.	$\frac{\mu v}{\mu D}$	Grm. Eq. Conductivity.
$\frac{1}{5}$	·431	1639
$\frac{1}{4}$	·495	1882
$\frac{1}{3}$	·532	2024
$\frac{1}{2}$	·583	2220
1	·629	2356
2	·681	25·92 / 25·95
4	·751	2860
10	·808	3074
20	·854	3265
40	·895	3417
80	·913	3500
200	·960	3656
1000		3820
2000		3806

Potassium Chloride.

Dilution Litres per Grm. Eq.	$\frac{\mu v}{\mu D}$	Grm. Eq. Conductivity.
$\frac{1}{10}$	·149	463
$\frac{1}{9}$	·161	502
$\frac{1}{8}$	·196	609
$\frac{1}{5}$	·313	978
$\frac{1}{2}$	·446	1441
1	·538	1726 / 1726
2	·628	1942
4	·695	2150
8	·739	2292
16	·794	2474
40	·834	2589
100	·854	2650
1000		3101

Potassium Nitrate.

Dilution Litres per Grm. Eq.	$\frac{\mu v}{\mu D}$	Grm. Eq. Conductivity.
$\frac{1}{6}$	·260	426
$\frac{1}{5}$	·268	446
$\frac{1}{4}$	·308	845
$\frac{1}{2}$	·411	1146
1	·486	1353
2	·546	1515 / 1521
4	·609	1695
10	·667	1854
20	·694	1933
40	·725	2020
80	·744	2072
300	·803	2234
1000		2540
2000		2483

Ammonium Sulphate.

Dilution litres per grm. Eq.	$\frac{\mu v}{\mu \Delta}$	grm. Eq. Cond = Conductivity.
.118	.164	45-9
.138	.198	904
.16	.205-	941
.25-	.250	1208
.5-	.304	1404
1	.343	1804 1804
2	.465-	2130
5-	.548	2509
10	.609	2784
20	.701	3291
50	.745-	3443
500	.868	4040
1000		4583
2000		4574

Potassium Iodide.

Dilution litres per grm. Eq.	$\frac{\mu v}{\mu \Delta}$	grm. Eq. Cond = Conductivity.
.233	.459	1800
.282	.496	1943
.5-	.599	2349
1	.645-	2546 2530
2	.733	2845-
4	.796	3118
8	.844	3306
16	.882	3457
80	.934	3641
300		3724
1000		3990
2000		3914

Ammonium Iodide.

Dilution litres per grm. Eq.	$\frac{\mu v}{\mu \Delta}$	grm. Eq. Conductivity
.2024	.303	1199
.224	.331	1309
.241	.370	1466
.285-	.394	1558
.5-	.588	2221
1	.660	2446
2	.728	2736
4	.798	3014
8	.852	3219
16	.875-	3305-
32	.912	3446
100	.966	3648
1000		3745-

Ammonium Hydroxide.

Dilution Litres per Grm. Eq.	$\frac{\mu_v}{\mu_\infty}$	Grm. Eq. Conductivity.
.184	.413	1540
.264	.474	1775
.333	.524	2083
.5	.599	2255
1	.655	2438
2	.721	2683
4	.786	2926
10	.851	3168
20		3373
40		3483
1000		3521

Lithium Hydroxide.

Dilution Litres per Grm. Eq.	$\frac{\mu_v}{\mu_\infty}$	Grm. Eq. Conductivity.
$\frac{1}{10}$	.151	440
$\frac{1}{7}$	.238	716
$\frac{1}{5}$	.314	985
$\frac{1}{2}$	.494	1534
1	.545	1686
2	.666	2068
5	.737	2289
10	.776	2409
1000		3102

Cadmium Iodide.

Dilution Litres per Grm. Eq.	$\frac{\mu_v}{\mu_\infty}$	Grm. Eq. Conductivity.
.312	.081	269
$\frac{1}{2}$	.098	324
1	.122	406
2	.154	500
5	.224	755
10	.296	984
1000		3314

Sodium Hydroxide

Dilution Litres per grm. Eq.	$\frac{\mu_v}{\mu_\infty}$	grm. Eq. Conductivity.
$\frac{1}{4}$	1444	.380
$\frac{1}{2}$	1811	.452
1	2085 2094	.525
2	2426	.645
4	2734	.719
10	2843	.761
20	3026	.801
3000	3744	

Part (3).

On experimental determination of the Boiling point elevation constant for dilute aqueous solutions and molecular weight determinations

1. Elevation Constant determined

In the tables given below values of the elevation constant were obtained from the formula*. $C = \frac{(E - OP)\ W}{w\ (1 + n - 1a)}$ with the best attainable degree of accuracy. The values of C. so obtained have been plotted against Ionization for several salts. The results obtained are given in the following tables and curves.

* Proc. Royal Soc Ed. 25 (11) 960 (1905). (Paper herewith p.960)

First Series.

Cadmium Iodide 15 c.c.s. Solution

grms. salt added.	Elec. Boiling point.	Per cent. composition.	grm eqv. per litre	Ionization Co-eff.	Elec. Constant
1	·228	·164	4·68	445	520
1	·4636	·218	10·40	639	516
2	·3840	·286	14·04	1·048	519
2	·9640	·354	16·80	1·210	521
3	·6850	·436	20·05	1·308	519
4	·3828	·514	22·44	1·563	522
5	·0616	·544	26·12	1·825	510
5	·8536	·682	28·41	2·021	526

Ammonium Chloride 15 c.c.s. Solvent.

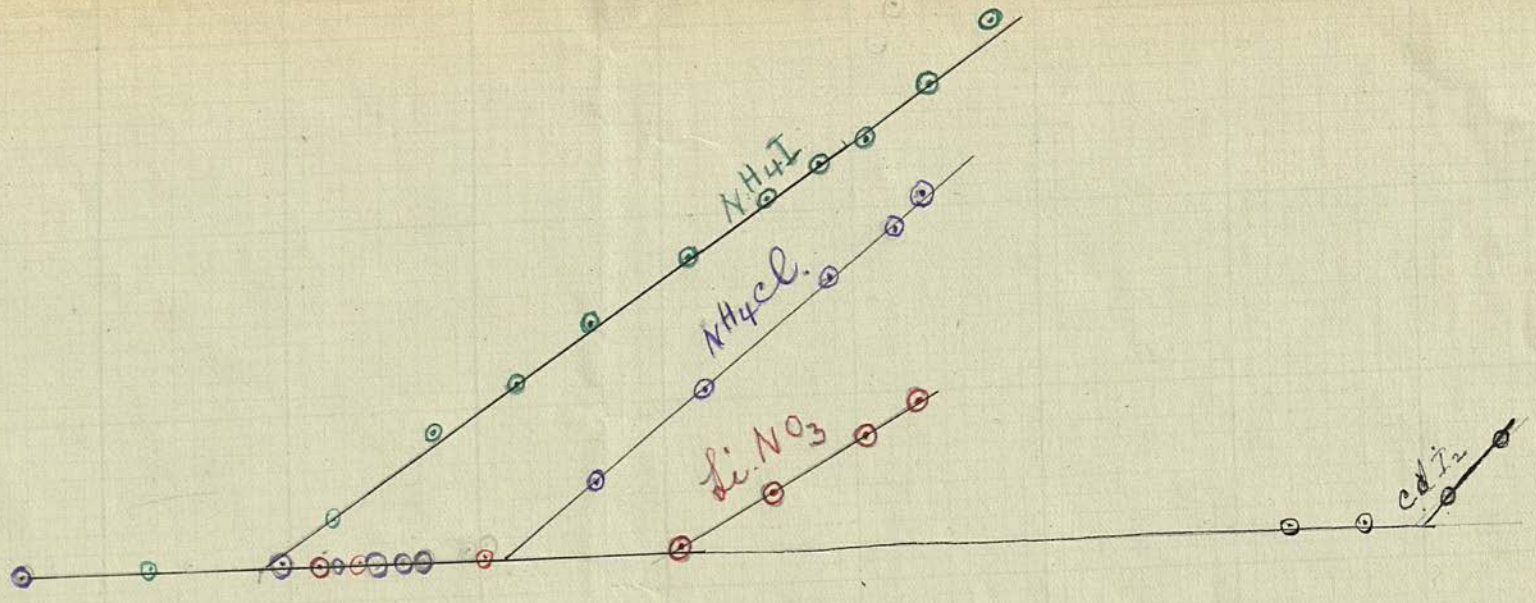
·1260	128	·850	·141	·844	520
·3422	363	2·26	·412	·704	522
·6552	543	4·26	·493	·653	518
·9604	960	4·94	·825	·650	520
·8430	842	5·61	1·055	·630	523
1·0446	1·046	6·65	1·255	·620	519
1·2812	1·329	8·01	1·531	·606	523

Sodium Iodide 15 c.cs.

grms. Salt added	Elec: Wt. Gel.	Per C. Comp.	grm. equiv: per litre	Ionization Co-eff.	Elec: Cond:		
.6600	.044	4.296	.232	.214	514	"	"
1.1440	.131	4.22	.413	.176	523	"	"
1.8258	.191	11.05	.655	.145	520	"	"
2.3248	.243	13.65	.855	.130	521	"	"
2.8564	.308	16.24	1.055	.119	519	"	"
3.4138	.381	20.14	1.350	.112	500	"	"
4.4524	.461	23.24	1.680	.104	503	"	"
5.1480	.556	26.05	1.838	.101	524	"	"

Lithium Nitrate 50. c.cs.

.1820	.103	.366	.041	.686	521
.5462	.193	1.092	.132	.648	524
.9032	.248	1.493	.284	.598	523
1.6328	.441	3.19	.433	.562	522
3.3490	.830	6.43	.921	.494	520
5.4310	1.164	10.22	1.50	.441	547
8.8354	2.128	15.15	2.26	.396	543
10.9336	2.656	18.10	2.721	.368	592


NH4I
NH4Cl.
Li.NO3
Cd.I2

From the curves it is apparent that a linear relation holds between the values of C and Ionization until a certain Ionization is reached which usually varies for different salts. Thereafter the curves change direction but seem to continue straight.

It has been pointed out by Professor Macgregor* that if the depression of the freezing point constant be plotted against Ionization the linear law holds to varying degrees of concentration, and for Sulphuric acid up to ·6 normal.

My observations show that to a greater concentration the linear relation holds from the elevation of the boiling point of view, in some instances to considerably higher concentrations, and for Cadmium Iodide to 1·8 N.

This would seem to indicate what Biltz[1] has found that from the elevation of boiling point, salts act more normally than from the depression of freezing point of view. At present we are only interested in dilute solutions, and for these in the value of the elevation constant for those concentrations for which it is constant.

From the tables and curves given above it is seen that this value is 520 (1 or 2 more or less.)** It will be seen later that this value of the elevation constant is that for all concentrations on the assumption of the Hydration theory

II. Molecular Weight Calculations.

We have[2] $m = \frac{C.w.(1 + n - 1a)}{W\,(E - OP)}$ See page (22)

The following calculations have been made from this formula, a few of these have already been given in Part (1).

* Phil. Meg. (1900) page 505.
1 Zeit. für. Phys. Chem. 40, 204. (1902).
2 Proc. Royal Soc Ed. 25, (11) 965. (1905). (Paper herewith)

xx. I have calculated the mean value of the elevation constant for the first cases, for each of the salts given in the Proc. Royal Soc Edinb. herewith which are 517.6 520.0 517.7 517.7 521.2. Their mean value being 518.8.

Potassium Bromide 50 c.cs. Solvent used.

grms. Salt added	Elec. % K. found	Per C. Comp.	grm. equiv. per litre	Ionisation co. eff.	Mole Weight	Molecular Weight Mean Value
						118·43
·4264	·120	·85	·092	·796	122·4	
·6854	·143	1·36	·132	·744	122·7	
·8813	·212	1·45	·164	·758	120·6	Recognised Value
1·0293	·238	2·03	·204	·774	118·4	118·99
1·2945	·262	2·53	·256	·732	118·0	
1·5405	·324	3·04	·308	·730	116·6	
1·9664	·386	3·88	·392	·706	116·2	
2·3044	·451	4·45	·442	·692	114·4	

Ammonium Chloride 15 c.c.s. Solvent used

Grms. Salt added	Elec. Eq. Pt.	Per C. Comp.	Grm. Equs. per litre	Ionization Co. eff.	Mole. Weight	Molecular Weight Mean Value
·1260	·128	·850	·141	·824	53·4	53·5
·3422	·363	2·26	·412	·702	53·8	Recognised Value
·6552	·543	4·26	·793	·653	54·1	53·5
·7604	·760	4·94	·825	·650	53·6	
·8730	·842	5·61	1·055	·630	51·9	
1·0446	1·046	6·65	1·255	·620	53·5	
1·2812	1·329	8·01	1·531	·606	54·5	
1·3620	1·662	9·60	1·852	·398	52·2	

2nd Series

Cadmium Iodide 15 C.C.S. Calcul-ated

Grms. Salt added	Elec. Conduct.	Per Cent Compo.	Grams Equiv. per litre	Ionization Co-eff:	Mole Weight	Molecular Weight Mean Value
1 ·228	·169	4 ·68	·445	·164	354 ·4	365 ·1
1 ·4636	·218	10 ·40	·639	·146	361 ·8	
2 ·3840	·286	14 ·04	1 ·048	·119	369 ·2	Recognized Value
2 ·4640	·354	16 ·80	1 ·210	·115	365 ·6	365 ·06
3 ·6850	·436	20 ·05	1 ·308	·113	364 ·2	
4 ·3828	·514	22 ·94	1 ·563	·104	364 ·8	
5 ·0616	·544	26 ·12	1 ·825	·101	342 ·9	
5 ·8536	·682	28 ·41	2 ·021	·096	361 ·9	

1. Series

Cadmium Iodide 15 c.c. Solvent used.

Grms. Salt added	Elec. & W. found	Percent Comps.	Grm Equs. per litre	Ionization Co-eff:	Mole Weight
·6600	·044	4 ·296	·232	·214	362 ·0
1 ·1440	·131	7 ·22	·413	·146	353 ·8
1 ·8258	·191	11 ·06	·655	·145	370 ·1
2 ·3248	·243	13 ·65	·855	·130	358 ·2
2 ·8564	·308	16 ·27	1·055	·119	360 ·0
3 ·4138	·381	20 ·14	1·350	·112	375 ·2
4 ·4524	·461	23 ·24	1·580	·104	340 ·8

Molecular Weight Mean Value
364 ·6

Theoretical Value
365 ·06

Potassium Iodide 15 c.c. Solvent used.

·4186	·351	4 ·66	·280	·768	173 ·1
2 ·5382	1·010	14 ·44	·962	·600	160 ·9

Molecular Weight Mean Value
167

Theoretical Value
165 ·99

Cadmium Bromide 50 c.c.s. Solvent-used

Grms. salt added	Elec. Ht. Point-	Per cent- Comp.	Grm. eqvs. per litre	Ionisation Co-eff.	Mole. Weight-	Molecular Weight- Mean Value
·9508	405	1 ·88	·199	·434	103·4	101·44
1·4200	544	2 ·78	·294	·704	103·3	
2·3200	699	4 ·47	·477	·644	103·0	Recognised Value
3·2544	781	6 ·16	·656	·610	101·0	102·01
4·3440	938	8 ·08	·840	·541	98·0	

Ammonium Sulphate 50 c.c.s. Solvent-water.

						Molecular Weight Mean Value
·4806	·136	1 ·353	·236	·536	131 ·4	131 ·6
·9590	·144	1 ·402	·294	·518	132 ·0	
1 ·2245	·215	2 ·414	·374	·496	132 ·3	Recognised Value
1 ·4358	·250	2 ·82	·436	·478	130 ·1	132 ·1
2 ·0126	·345	3 ·91	·612	·438	132·0	

Lithium Nitrate 50 c.c.s. Solvent used.

grms. Salt added	Elec. Ø K. point.	Per cent. Comps.	grms. equiv. per litre	Ionisation Co-eff.	Mole. Weight
·1820	·103	·366	·041	686	68·4
·3462	·193	1·09	·132	648	68·0
1·9032	·278	1·493	·284	·598	68·3
1·6328	·441	3·19	·433	·562	68·4
3·3490	·830	6·43	·921	494	68·8

Molecular Weight Mean Value
68·4

Recognised Value
68·9

Ammonium Bromide 15 c.c.s. Solvent used.

4·134	·245	2·435	·368	·754	100·1	Molecular Weight Mean Value.
·842	·542	5·424	·749	·688	96·3	98·2
						Recognised Value 98·0

Cadmium Nitrate 50 c.c.s. Coloured-used.

grms. Cad-adada	Per cent Coccup:	grm. equv. Per litre.	Elc: of Gr. facil-	Ionisation CO = eff:	Mole: Weight-	
						Molecular Weight-
·2064	·36	·042	·053	·84	86	Mean Value -
·4860	·87	·105	·111	·82	84	84·4
1·0198	1·81	·218	·220	·76	84	Recognised Value
1·4880	2·50	·302	·312	·70	86	86·08
1·9852	3·60	·435	·420	·65	85	
2·5216	4·80	·578	·530	·62	82	
3·0242	5·34	·664	·632	·59	80	
3·5682	6·58	·744	·700	·54	83	

Potassium Chloride 50. c.c.s. Solvent used

Grms. Salt added.	Per Cent. Comps.	Grm. Mgs. per litre	Elev. B. Pt.	Solubility Co-eff:	Mole: Weight	Molecular Weight — Mean Value.
·1754	·35	·048	·054	·89	73	
·3546	·71	·124	·101	·88	73·3	74·83
·5424	1·08	·144	·146	·84	76	Recognised Value
·7426	1·47	·202	·190	·85	76	74·59
·9440	1·93	·266	·244	·83	76	
1·1520	2·26	·316	·291	·81	76	
1·3684	2·69	·370	·343	·79	76	
1·5924	3·11	·428	·394	·77	74	
1·7248	3·34	·466	·425	·76	74	
1·8918	3·68	·508	·441	·76	74	

Potassium Nitrate 50 c.cs. Solvent used.

Grams. Salt added	Per C. Comp:	Grm: Eqvs: per litre	Elev: B. Pt.	Ionisation Co-eff:	Mole: Weight	
						Molecular Weight
·2118	·42	·041	·063	·665	101	Mean Value
·443	·89	·089	·112	·654	104	101·2
·6986	1·39	·139	·160	·642	102	Recognised Value
·9318	1·85	·184	·206	·629	99·4	101·14
1·2126	2·39	·244	·252	·616	100	
1·5044	2·95	·301	·292	·611	103	
1·8366	3·54	·364	·348	·608	103	
2·1876	4·23	·431	·403	·605	111	

Summary of Molecular Weights found.

Name of Salt.	Mol: Weight Experimental Value.	Mol: Weight Recognised Value.
Potassium Nitrate,	101 · 2	101 · 14
Potassium Hydroxide,	118 · 43	118 · 44
Ammonium Chloride,	53 · 5	53 · 5
Cadmium Iodide.	365 · 1	365 · 06
" "	364 · 6	365 · 06
Potassium Iodide	164	165 · 99
Sodium Hydroxide	101 · 44	102 · 01
Ammonium Sulphate	131 · 6	132 · 1
Lithium Nitrate	68 · 4	68 · 9
Ammonium Bromide	98 · 2	98 · 0
Sodium Nitrate	84 · 4	85 · 8
Potassium Chlorate.	74 · 83	74 · 3-9

Part (4).

Concentrated Solutions.

We now come to the study of concentrated solutions. At first from the standpoint of values of the so called elevation constant and afterwards from that of determining the meaning of the results obtained.

The following results have been obtained by the use of the formula $C = \frac{m.\ W.\ \Delta E}{(1 + n - 1a)\ \Delta W}$ from experimental data.

Where

m = Molecular weight of salt added.

W = weight of solvent used in grammes.

ΔE = Increment of elevation of boiling point when salt is added to a solution.

ΔW = Increment of weight of salt added in grammes.

a = ionization coefficient.

n = number of free ions into which a molecule of salt dissociates.

A tube for 15 C.cs of solvent was used so that high concentrations were quickly obtained and in consequence we have only a very few observations for dilute solutions. It was impossible therefore as a rule to draw the curves with grammes of salt added as ordinates and elevation of boiling point as abscissae so accurately in the neighbourhood of the origin, as when dilute solutions were specially under consideration. In consequence a less degree of accuracy must be expected in values obtained for the elevation constant for the dilute solutions than when the latter were being dealt with specially. The error involved in consequence although it creates a somewhat large percentage error for the dilute solutions is usually under one hundredth of a degree which for concentrated solutions where the elevation is from three to ten or more degrees would only be one in from three to ten hundred and consequently negligible, the more so because at these concentrations it is not supposed the ionization coefficients are more than rough approximations. At the same time it should be remembered that when determining values of the elevation constant, it is $1 + n - 1a$ which is used, so that ~~(only a fraction of)~~ the error in the value of ionization coefficients which came into the results was very much less significant.

Sodium Chloride 25 c.c.s. Solvent.

Grms. salt added.	Per cent. composition.	Grm. eqs. per Litre.	Elevation & Boiling point.	Ionization Co = eff.	Elec. Conductivity
·1314	·64	·141	·094	·854	301
·3266	·96	·203	·198	·804	496
2·0520	4·20	1·38	1·332	·612	578
2·2438	4·94	1·52	1·482	·602	581
2·3448	8·20	1·58	1·619	·596	595
2·4424	4·66	1·84	1·842	·542	610
2·8424	10·35	1·96	1·941	·562	624
3·1325	10·88	2·08	2·132	·552	632
3·3805	11·76	2·26	2·313	·538	634
3·6801	12·48	2·44	2·531	·522	656
3·8341	13·30	2·52	2·689	·516	666
3·9889	13·81	2·62	2·818	·508	642
4·1247	14·40	2·70	2·936	·502	684

Ammonium Chloride 25 c.c.s. Solvent.

·1480	·414	·123	·129	·498	506
·3396	1·35	·231	·231	·754	504
·4688	3·40	·642	·513	·666	523
1·20824	4·66	·895	·812	·640	538
1·8144	6·83	1·30	1·212	·614	543
2·5212	9·25	1·78	1·616	·592	566
3·0506	10·98	2·14	1·960	·542	532
3·6042	12·4	2·48	2·333	·556	546
4·0198	13·9	2·72	2·638	·544	560
4·5244	15·4	3·02	3·004	·528	569
4·9094	16·5	3·24	3·184	·514	563

Potassium Nitrate 15 c.c.s Solvent

Saturated Solutions

Grms. Salt added.	Per cent Composition.	Grm x eqs. per Litre.	Elevation of Boiling point.	Ionization Co = eff.	Elec. Conductance.
3698	2·45	·312	·264	·382	
1·1922	4·50	1·215	·841	·454	
2·0496	12·34	2·025	1·516	·406	530
2·9666	16·85	2·988	2·241	·386	533
3·7660	20·40	3·341	2·918	·338	588
4·9920	24·82	4·118	3·921	·316	605
5·5344	27·36	4·62	4·428	·280	639
7·0466	32·41	5·39	6·160	·262	702
8·2510	35·95	5·98	7·200	·256	715
9·5464	39·34	6·52	8·496	·252	720

Potassium Nitrate 50. c.c.s. Solvent.

Dilute Solutions.

·1820	·366	·041	·103	·686	521
·5462	1·092	·132	·193	·648	524
·9032	1·793	·284	·244	·598	523
1·6328	3·19	·433	·441	·562	522
3·3940	6·43	·921	·830	·494	520
5·4310	10·22	1·50	1·164	·441	547
8·8354	16·15	2·26	2·128	·396	573
10·9336	18·10	2·721	2·656	·388	592

Cadmium Iodide 15 c.c. Solvent.

grms. salt added.	Percent: composition	grm. eqs. per Litre.	Elevation of Boiling Point	Ionization Co-eff.	Elec. Conduct.
.6600	4.296	.232	.044	.214	5.14
1.1440	7.22	.413	.131	.146	5.23
1.8258	11.05	.655	.191	.145	5.20
2.3248	13.65	.855	.243	.130	5.21
2.8564	16.24	1.055	.308	.119	5.19
3.4138	20.14	1.350	.381	.112	5.00
4.4524	23.24	1.580	.461	.104	5.03
5.1480	26.05	1.838	.556	.101	5.24
5.9198	28.42	2.125	.633	.094	5.26
6.6506	31.16	2.388	.725	.089	5.38
7.3846	33.45	2.625	.824	.083	5.54
8.1910	35.78	2.859	.925	.078	5.62
8.9688	37.90	3.101	1.022	.073	5.71
9.7522	42.15	3.648	1.049	.059	5.75

Lithium Hydroxide 15 c.c.s. Solvent.

.3122	2.079	.262	.274	.718	5.18
.6352	4.142	.584	.532	.654	5.62
.9450	6.228	.764	.791	.608	5.95
1.3230	8.258	1.051	1.085	.564	630
1.6108	9.89	1.260	1.428	.548	665
2.0858	12.43	1.549	1.798	.526	698
2.4926	13.33	1.731	2.199	.492	736
2.9192	16.54	2.243	2.695	.446	782
3.3126	18.39	2.732	3.141	.448	859
3.7698	20.42	2.945	3.741	.434	874
4.2190	22.31	3.286	4.359	.416	920
5.1444	26.05	3.94	5.765	.376	1026
6.1692	29.54	4.48	7.421	.344	1136

Ammonium Iodide 15 c.c.s. Solvent.

Grms. Salt added.	Per cent. composition	Grm. eqs. per litre.	Elevation of Boiling point.	Ionization co-eff.	Elec. Conduct.
.5498	3.42	.260	.290	.744	524
1.4398	10.58	.745	.490	.648	5.23
2.4860	15.9	1.226	1.250	.624	5.88
3.8908	20.10	1.624	1.460	.548	610
4.9696	25.2	2.055	2.335	.534	642
6.0348	29.1	2.446	2.846	.488	674
7.0862	32.5	2.805	3.392	.444	706
8.0540	35.4	3.140	3.840	.416	722
9.1206	38.2	3.458	4.344	.390	733
10.2102	40.9	3.749	4.950	.356	761
10.4614	42.3	3.946	5.361	.352	784
13.3904	51.1	4.714	7.664	.322	796
17.5818	54.4	5.150	8.700	.292	809
19.1904	56.6	5.83	9.568	.262	840
20.1800	54.8	5.94	10.154	.256	852

Potassium Iodide 15 c.c.s. Solvent.

1.0312	6.55	.515	.394	.732	500
2.2370	13.15	.849	.866	.642	543
3.5122	19.28	1.368	1.350	.650	593
4.4084	23.08	1.695	1.721	.610	600
5.3046	26.53	1.948	2.146	.594	630
6.4266	30.44	2.060	2.644	.555	663
7.3928	33.4	2.665	3.184	.541	691
8.5136	36.84	2.965	3.658	.525	712
9.6638	39.64	3.341	4.360	.508	740
10.6884	42.11	3.660	4.901	.490	765
12.4741	45.9	4.16	5.955	.462	782
14.4442	49.5	4.62	6.709	.436	800

Ammonium Sulphate 25 C.C.S. Solvent

Grms. Salt added.	Per cent composition.	Grm. eqs. per litre.	Elevation of Boiling point.	Dissociation Co-eff.	Elec. Conduct.
2.351	.944	.141	.081	.546	526
1.3148	5.04	.860	.398	.416	526
8.1906	24.8	4.34	2.132	.242	591
11.3674	31.4	5.52	3.014	.202	606
15.7030	38.8	6.50	4.298	.196	651
16.4862	39.9	6.94	4.576	.194	666
17.2096	41.0	7.10	4.979	.192	682
18.0360	42.1	7.22	5.314	.188	700
18.9242	43.3	7.32	5.374	.186	678
20.2898	44.1	7.46	5.608	.184	647
22.1284	47.2	7.84	5.822	.182	644
23.9964	49.2	8.34	6.258	.176	629

Lithium Chloride 15 C.C.S. Solvent

.1514	1.01	.250	.231	.696	516
.5718	3.74	.922	.743	.568	522
1.0162	6.46	1.28	1.592	.534	633
1.5220	9.38	2.23	2.547	.462	710
1.9398	11.66	2.87	3.438	.426	776
2.4426	14.26	3.60	4.649	.384	856
2.9072	16.51	4.25	6.014	.344	959
3.4228	18.88	4.70	7.542	.322	1009
3.9494	21.18	5.31	9.294	.294	1133
4.5394	23.60	5.98	11.419	.264	1243

Ammonium Bromide 15 c.c.s. Solvent.

Grms. Salt added.	Per cent. composition.	Grm. eqvs. per Litre.	Elevation of Freezing point.	Ionization Co-eff:	Elec. Constant.
·4134	2·735	·368	·245	·954	509
·8424	5·427	·749	·542	·688	529
1·2940	8·11	1·09	·814	·646	534
1·7148	10·45	1·42	1·046	·626	545
2·1324	12·64	1·74	1·345	·606	554
2·5278	14·64	2·14	1·596	·586	567
2·9588	16·76	2·29	1·841	·564	577
3·8112	20·59	2·83	2·436	·533	584
4·6946	24·22	3·34	2·968	·518	595
5·5134	27·28	3·77	3·511	·482	610
6·8608	31·8	4·41	4·431	·452	623
7·8588	34·8	4·83	5·003	·434	638
9·7250	39·8	5·63	6·224	·414	645
10·5634	41·8	5·81	6·654	·376	656

Ammonium Iodide 25 c.c.s Solvent.

·3472	1·38	·105	·082	·854	506
1·1884	4·68	·354	·272	·764	510
3·2344	11·56	·899	·805	·664	542
4·6652	15·8	1·233	1·198	·624	542
6·0546	19·6	1·533	1·608	·592	602

These results show that when values of the elevation constant are calculated according to the formula used there is a very decided increase in its value with concentration. To what is this due? It has already been shown that it is not accounted for by error in the Barometric readings. Through comparing different series on the same salt, and the reheating of the same solution on several occasions, it became evident also that overheating of solutions was not the cause of the high values. Duplicate series for the elevation constant giving high values were obtained for Na Br. these are given graphically on page (6) the following are the values obtained for the elevation constant.

1st Series	5.12	5.90	6.15	6.26	*
2nd Series	5.05	5.79	6.01	6.57	

When taking the observations for these results, the greatest care was taken to avoid overheating. It would not therefore appear that this is the cause of the high values obtained. There remains another possible explanation worthy of testing. It is, that the ion and molecule may have very different values for the elevation constant. So much might be indicated by the fact that for dilute solutions C. approaches one value, for concentrated solutions it increases with the concentration on the assumption (of the amount of active water being constant) pointed out on page ( ). In the one case there are few molecules present in the other comparatively few ions. Such an idea was strengthened by the fact that for several salts at the same ionization and at a not very different concentration, nearly equal values of the elevation constant were obtained. To test this explanation I turned to non electrolytes to see what values of the elevation constant these would give. Here molecular values of the constant are obtained there being little or no ionization, Except in one or two instances these were not large to anything like the extent the above explanation would require.

* As the boiling tube used was a 15 c.c. one considerable concentration was reached quickly. Rectification has not in consequence been so accurate as in some instances before.

Testimony of Cadmium Iodide.

CdI_2 is an electrolyte which dissociates slightly at ordinary concentrations. We should expect therefore on the above explanation that high values of the elevation constant would be obtained for these On the contrary ordinary values of the constant were obtained and that for duplicate series. These are given graphically on page ( )
The following are the values obtained.

1st Series. 514, 523, 520, 521, 519, 500, 503, 524, 526.

2nd Series. 520, 516, 519, 521, 519, 522, 510, 526.

These several results in combination show that largely different values for the ion and the molecule are not the cause of the increase of the elevation constant with concentration.

Having shown that the high values obtained for the elevation constant are not due to any of the suppositions put forward. We come to study hydration. On this theory the values referred to are due to combination of water molecules with salt ions or molecules thereby removing so much water from the field of action, and reducing the amount of active solvent by just so much.

The theory tested from the standpoint of results.

We have* $C = \frac{m W (E - OP)}{(1 + N - la) W}$ (1)

If C^1 be the value of the so called constant obtained at a certain concentration. Then $C^1 = \frac{m W (E - OP)}{(1 + N - la) W_1}$ (1)

The hydration theory gives $C = \frac{m W^1 (E - OP)}{(1 + N - la) W}$ (2)

When W^1 is the amount of active water in the solution at the concentration, that is the amount of water not in a state of combination with salt, and C is the theoretical value of the constant. We have therefore dividing (2) by (1) $\frac{C}{C^1} = \frac{W^1}{W}$

or $W^1 = W \cdot \frac{(C)}{(C^1)}$ (3)

$$W - W^1 = W \frac{(C^1 - C)}{C^1} \quad (4)$$

This equation may be put in another form.

Form (2) We have $W^1 = \frac{(1 + N - la) \cdot WC}{m (E - OP)}$ (5)

The water in a state of hydration $= W - W^1$

* Proc Royal Soc. Vol XXV (11) 960. (1905).

To obtain the number of molecules of hydration per molecule or ion on the assumption that both molecules and ions hydrate.

If W and w be weight of solvent and of salt added to the solvent respectively W^1 the active or uncombined water and the ionization coefficient at the concentration.

Then $\frac{W - W^1}{18}$ is the number of gramme molecules of solvent present.

And $W \frac{(1 + n - 1a)}{m}$ is the number of gramme particles (molecule or ion) of salt present.

The ratio gives the number of molecules of water per molecule or ion of salt in solution.

The number of molecules of water per molecule or ion of salt therefore is equal to $\frac{(W - W^1)\, m}{18\, w\, (1 + (n - 1)\, a)}$

The ionic hydration on the assumption that ions only hydrate is

$$\frac{(W - W^1)\, m}{18,\ n,\ a,\ w.} \qquad (6)$$

Were the hydration only molecular the formula becomes

$$\frac{(W - W^1)\, m}{18\ (1 - a)\ w} \qquad (7)$$

(The value of a for concentrated solutions are not supposed to be more than rough approximations.) X

In the tables given below:-

"Mol. Hyd" stands for the number of molecules of water combined with one molecule of salt, on the assumption that only molecules hydrate

"Ionic Hyd." stands for the number of molecules to one ion on the supposition that only ions hydrate.

"Mol Ionic Hyd" stands for the hydration per molecule or ion on the assumption that both hydrate, for the moment assuming that the hydration per ion or molecule is the same.

The figures under "Hydration" indicate the number of grammes of combined water which are in a state of hydration or taken up by the salt particles.

x. The full force of this error would come into the ionic hydration calculations. It would be less represented in the molecular hydration and very much less in the molecular ionic hydration.

Ammonium Sulphate 25 ccs. Solvent.

Grm. eqs. per Litre.	Grms. Hydration Water.	Mol. or Ionic Hydration.	Ionic Hydration.	Molecular Hydration.
.860	1.0	.022	2.2	1.7
4.34	3.5	1.2	2.3	1.8
5.52	4.4	1.0	2.3	1.7
6.50	5.9	1.0	2.0	1.6
6.94	6.3	1.0	2.5	1.7
7.10	6.7	1.0	2.4	1.5
7.22	7.2	.9	2.5	1.8
7.32	6.6	.9	2.3	1.5
7.46	5.7	.75	1.8	1.2
7.84	5.5	.71	1.6	1.1
8.34	4.7	.48	1.6	.68

Strontium Nitrate 15 c.cs. Solvent.

2.025	.3	.38	.66	.88
2.788	.9	.84	1.5	1.9
3.371	1.7	1.2	2.8	2.6
4.118	2.1	1.2	2.4	2.3
4.62	3.1	1.5	3.9	3.0
5.34	3.9	1.6	4.0	2.8
5.98	4.1	1.5	3.6	2.5
6.52	4.1	1.3	3.3	2.2

Cadmium Iodide 15 c.cs. Solvent.

1.838	.2	.3	1.3	.4
2.125	.2	.3	1.2	.4
2.388	.5	.6	3.0	.8
2.625	1	1.3	6.7	1.4
2.859	1.1	1.2	7.4	1.4
3.101	1.3	1.2	7.2	1.6
3.648	1.3	1.4	7.9	1.4

Lithium Chloride 15° C.C.S. Solvent.

Grm. eqv. per litre.	Grms. Hydration Ratio.	Mol. or Ionic Hydration	Ionic Hydration	Molecular Hydration
1.28	2.4	3.1	6	13
2.23	4.0	4.2	6	11
2.84	4.4	4.0	4	10
3.60	5.8	4.0	4	4
4.25	6.8	4.1	4	8
4.70	4.2	4.0	4	4
5.31	8.0	3.6	8	6
5.98	8.6	3.5	8	6

Potassium Iodide 15° C.C.S. Solvent.

.849	.4	1.4	2.1	9.5
1.368	1.4	2.2	2.8	10.
1.695	2.0	2.6	3.5	10.9
1.948	2.6	2.8	4.1	12
2.050	3.2	2.9	4.2	10.4
2.665	3.4	3.0	4.8	10.2
2.965	4.0	2.9	4.2	9.2
3.341	4.4	2.8	4.1	8.4
3.660	4.8	2.8	4.2	8.5
4.16	4.9	2.6	4.0	6.8
4.62	5.2	2.3	3.8	5.4

Ammonium Bromide 25° C.C.S. Solvent

3.46	4.5	1.3	2	4.4
4.24	5.3	1.4	2.1	4.4
5.30	6.4	1.2	1.9	3.4
5.46	6.9	1.2	1.9	3.3
5.34	7.1	1.1	1.9	3.3

Lithium Bromide 15° C.C.s. Solvent.

Grm. eqv. per Litre.	Gross Hydration Water.	Mol. or Ionic Hydration.	Ionic Hydration.	Molecular Hydration.
·584	1·1	5·0	6·2	30
·764	1·4	5·8	7·3	26
1·051	2·6	6·2	8·4	24
1·260	3·1	6·1	8·6	21
1·549	3·8	5·9	8·4	19
1·731	4·4	5·8	8·7	17
2·243	5·0	5·6	8·9	15
2·732	5·5	5·5	9·0	14
2·945	6·0	5·3	9·0	13
3·286	6·4	5·2	9·0	12
3·94	7·2	5·0	9·0	10
4·48	8·0	5·2	9·1	9·8

Ammonium Chloride 15° C.C.s. Solvent.

1·852	·3	·36	·5	1·4
2·345	·4	·60	·92	2·3
2·849	1·0	·80	1·1	2·6
3·338	1·6	1·0	1·5	3·2
3·922	2·1	1·2	1·7	3·3
4·365	2·6	1·1	1·9	3·1
5·042	2·9	1·1	2·0	3·0
5·412	3·2	1·2	2·0	2·9
6·022	3·4	1·0	1·5	1·9
6·420	3·9	1·1	1·3	1·6

Ammonium Iodide 15 c.cs. Solvent.

Grm. eqs. per Litre.	Grms. Hydration Water.	Mol. or Ionic Hydration.	Ionic Hydration.	Molecular Hydration.
1·226	1·4	3·0	2·4	13·4
1·624	2·2	2·4	3·4	11·0
2·055	2·4	3·0	4·4	10·4
2·446	3·4	3·0	4·4	8·4
2·805	3·4	3·0	5·0	7·4
3·140	4·6	3·2	5·3	7·4
3·458	4·5	2·4	5·0	6·2
3·744	4·4	2·4	5·2	5·5
3·946	5·0	2·6	5·3	5·4
4·114	5·1	2·2	4·1	4·5
5·150	5·4	2·0	4·2	4·1
5·83	5·6	1·4	4·5	3·1
5·94	5·2	1·4	4·0	2·4

Ammonium Iodide 25 c.cs. Solvent.

·894	1	1·5	2·5	8
1·233	2·3	2·8	3·2	10·6
1·533	3·6	3·0	4·4	11·4

Lithium Nitrate. 50 c.cs. Solvent.

1·50	1·4	·89	1·4	2·2
2·26	4·6	1·4	2·4	3·4
2·721	6·1	1·5	2·4	3·38

Sodium Chloride 25 c.c.s. Solvent.

Grm. eqv. per litre.	Grms. Hydration Water.	Anal. or Ionic Hydration.	Ionic Hydration.	Molecular Hydration.
1·38	3·4	3·3	4·3	13·4
1·52	3·5	3·1	4·2	13·5
1·58	3·8	3·2	4·3	12·0
1·84	4·1	3·0	4·2	11·0
1·96	4·4	3·1	4·4	11·6
2·08	4·7	3·2	4·4	11·3
2·26	5·2	3·2	4·6	11·0
2·44	5·5	3·2	4·6	10·1
2·52	5·8	3·1	4·8	10·0
2·62	6·0	3·2	4·9	9·6
2·70	6·5	3·4	5·1	10·0

Ammonium Nitrate 15 c.c.s. Solvent.

·749	·3	1·2	1·4	8·0
1·09	·5	1·2	1·5	6·7
1·42	·7	1·3	1·8	6·5
1·74	1·0	1·6	2·1	6·4
2·14	1·2	1·6	2·1	6·5
2·29	1·5	1·7	2·3	6·3
2·83	1·7	1·6	2·2	5·4
3·34	1·9	1·4	2·4	4·5
3·77	2·2	1·3	2·3	4·1
4·41	2·5	1·3	2·2	3·6
4·83	2·8	1·3	2·2	3·4
5·53	2·9	1·1	2·0	2·7
5·81	3·1	1·1	2·1	2·5

First Series.

Sodium Hydroxide 25 c.c.s. Solvent.

Gram. eqs. per Litre.	Gram. Hydration Water.	Mol. of Ions Hydration.	Ionic Hydration.	Molecular Hydration.
1·14	2·4	3·4	4·9	11
1·40	4·0	3·2	4·8	10
2·05	4·4	3·1	4·8	8·4

Second Series Concentrated Solutions 50 c.c.s.

5·21	10·3	1·8	3·4	3·4
5·34	10·2	1·8	3·6	3·5
5·43	10·5	1·4	3·5	3·5
5·33	11·0	1·4	3·4	3·4
5·61	11·1	1·4	3·4	3·3

Looking at the results obtained we see that the maximum ionic hydration is greater for Potassium Bromide, than Potassium Iodide. The ionic hydration for Sodium Chloride is greater than that for the Bromide for Lithium the chloride also is greater than for the Bromide. And for Lithium nitrate the maximum ionic hydration is less than that for either the Bromide or Chloride. These results would therefore indicate the hydration order in ascending magnitude to be n nitrate, Iodide, Bromide, Chloride.

So far as these ions are concerned a corresponding indication has been obtained by an electrolytic method.[1]

[1]Gerrard and Opperman have found that the cl ion takes up four molecules of water, the Bromine ion four, the No_3, two and one half and the So_4, five molecules. On the assumption that the H, ion does not hydrate. [2]Jones and Getman have found that in a threefold normal solution of Hcl, every molecule dissociated or not takes up eight molecules of water. For $H_2 So_4$ Jones* has shown that in dilute solutions it hydrates as $H_2 So_4$, H_2O. in more concentrated solutions as $H_2 So_4$, $2H_2O$.

1 Gottinger Nachrichten p 85 (1900) (see page 55)
2 Am. Chem. Jo. 30, 308 (1904)
* " " " 16, 1 "

The results ~~just~~ given above indicate that on the supposition of the theory of hydration the quantity of combined water increases with concentration with a greater degree of regularity than one would expect considering that into every final result various experiments and curve readings entered. As to the results under the various forms of hypothetical hydration, these give room for selective choice.

*Lewis who says--"From the laws of mass action hydration should decrease"[II] will no doubt choose molecular hydration as the more probable in as much as on this hypothesis almost from the appearance of hydration right along through all concentrations there is a decrease of hydration per molecule. Others will with equal certainty think there is no competition for water amongst the ions or molecules or both until high concentrations are reached if even then, there being throughout the concentrations, as a rule, grammes of unhydrated water in solution.

These will look more favourable on the ionic or ionic molecular theories of hydration.

Some may be disposed to say that the one which is the most constant in hydration is the more probable, perhaps this would be the ions.

If the ions only hydrate then some of the numbers which have been obtained indicate that they hydrate in different proportions, round numbers, although sometimes obtained, not being general for the maximum hydration. The hydration per ion in the case of salts like Na cl. would be the sum of two equal or two unequal ~~quantities~~ valencies, namely the hydration for each ion divided by two. If this be the true hydration theory the question of ionic hydration valencies should be speedily settled.

But if on the other hand, molecules and ions each hydrate and that in all cases, then the hydration question becomes much more complex and with increased difficulty the valency question will be settled.

At this stage, the theory will have to pass through a somewhat severe test, as one result is compared with another.

Do the ions, or molecules, or both, hydrate? The answer which

[1]Jones / One is inclined to think he is right as the question is one of valency

* Zeit für phys. Chem. 52, 224. (1905)
[1] Am. Chem. Jo 31 P 356, (1904)
II Nernst does not think the massaction law has anything to say on the point.

Jones and Getman give to this question is-"It is difficult to say whether it is the molecules or the ions or both that form the hydrates in concentrated solutions, since all such solutions that we have studied contain both molecules and ions. Since however these solutions that are most concentrated and therefore the least dissociated show the greatest amount of hydration it seems probable that it is the molecules and not the ions that combine with water and form hydrates."

Jones and Getmann found their idea on the fact that the more concentrated solutions are those in which hydration is greatest. Wherethere are relatively few molecules there is no hydration. If one were only to consider a single salt or a few salts of the same kind, preferably those which ionize highly then one might, probably would, see ground for their conclusion, but when salts which ionize very differently are considered it is seen that those which ionize highly as a rule, commence to hydrate at the smaller concentration and it is these which haye the fewer number of molecules at this concentration, and many times less molecules in solution than those which ionize less, when these commence to hydrate.One sees therefore that in case many ions are immediately formed hydration commences in dilute solutions and that where the salt ionizes feebly a greater concentration is reached, sometimes very much greater* This indicates that the commencement of hydration is dependent on the number of ions in solution, not at all on the number of molecules, and indicates that the ioms hydrate.

With regard to the non electrolytes, [1]Roth finds that for various non electrolytes considered there is a disagreement of about .2 per cent with the depression constant the meaning of which is that so far as his observations went there was no hydration. [2]P. W. Robertson with regard to the Esters in Phenal solution finds "that they have either a high initial depression and a negative rate of association or associate /

*
1 Jo. Chem. Soc. (Oct 1905).
2 Ztshr. phys. Chem. 43, 539 - 564. (1903)

associate slightly in dilute solutions and thus exhibit a minimum." Although these results were obtained from Phenal as solvent nevertheless they are interesting from the standpoint of hydration.

*Loomis, found for non electrolytes "that depression of the freezing point is either the same at all concentrations or changes gradually when referred to one thousand grammes of the solvent.

These results indicate that some non-electrolytes hydrate others do not.

The results I have obtained for non-electrolytes confirm those of Loomis and Roth, and Robertson. (See next page). 54.a

In this respect perhaps the electrolytes resemble the non-electrolytes, in some instances their molecules hydrate in others not.

On the question of ionic hydration the results of [1]Gerrard and Opperman are interesting.

It has been pointed out that the value of the elevation of boiling point constant does not change its apparent value by the ordinary method of computation until a certain ionization is reached. This is in harmony with the minima of various observers in curves when the equivalent depression of freezing point is plotted against equivalent concentration and in the curves when equivalent elevation is plotted against equivalent concentration as given by [2]Biltz, [3]Jones, Getman and those obtained by [4]myself. Each indicates that there is no hydration in dilute solutions. On this point [5]Jones and Getman say:- "In the dilute solutions there is no evidence of the existance of hydrates." The minima are illustrated by the following tables and curves. More curves would have been drawn but for their lying so close together. (See page 55)

* Phys. Rev. 12 220, 1901.
1 Sammlung Chemisher Vortrage page 39 band VIII (1903)
1 Gottinger Nachrichten page 86, (1900)
3 American Chem. Jo. 31, 325, (1904)
4 Page ( )
5 Am chem Jo. 31 355. (1904)
2 Zeit fur p Chem 40 209 (1902)

Mannitol $C_6H_8(OH)_6$

Grms. Salt added.	Elec. % Dissoc.	Elec. Constant.
.4808	.143	5.30
.9552	.141	5.36
1.4346	.190	5.36
1.8936	.226	5.35
2.3536	.254	5.30
2.7486	.278	5.34
3.2046	.305	5.36
3.8536	.344	5.34
4.2482	.364	5.34
4.7340	.396	5.38
5.3946	.424	5.34
5.8546	.454	5.34
6.3432	.490	5.38
6.8642	.520	5.35

Cane Sugar $C_{12}H_{22}O_{11}$

Grms. Salt added.	Elec. % Dissoc.	Elec. Constant.
.2500	.045	8.55
.7238	.095	9.38
1.1906	.189	9.69
1.8944	.224	9.68
2.5644	.289	9.98

Boracic Acid $B(OH)_3$

.7516	.131	5.20
2.2096	.512	5.32
4.4920	.911	5.61
7.9572	1.485	5.62

Tartaric Acid.

Grms. Salt added.	Elec. % Dissoc.	Elec. Constant.
.2566	.033	489
1.1542	.168	5.41
2.3444	.344	5.45
3.2162	.484	5.59
4.5206	.684	5.63
6.8758	1.049	5.82
8.4946	1.349	5.88

In these tables η = the number of grm. eqs. per litre.

Ammonium Iodide.

grm. eqs. per litre.	Elec. of Boiling point.	$\frac{C}{\eta}$
·260	·290	1·11
·445	·440	1·01
1·220	1·250	1·02
1·624	1·760	1·08
2·055	2·335	1·13
2·446	2·846	1·16
2·805	3·342	1·20
3·140	3·840	1·23
3·458	4·374	1·26
3·749	4·950	1·30
4·414	7·664	1·62
5·83	9·568	1·64
5·94	10·154	1·76

Ammonium Bromide.

grm. eqs. per litre.	Elec. of Boiling point.	$\frac{C}{\eta}$
·368	·245	·74
·749	·542	·72
1·09	·814	·74
1·42	1·046	·73
1·74	1·345	·77
2·04	1·596	·78
2·29	1·841	·81
3·34	2·468	·88
3·77	3·511	·93
4·41	4·431	1·00
4·83	5·003	1·03
5·58	6·224	1·12
5·81	6·654	1·14

Cadmium Iodide.

grm. eqs. per litre.	Elec. of Boiling point.	$\frac{C}{\eta}$
·232	·074	·33
·413	·131	·314
·655	·191	·291
·855	·243	·285
1·155	·308	·266
1·350	·381	·282
1·580	·461	·290
1·838	·556	·302
2·388	·725	·303
2·625	·824	·313
2·869	·925	·322
3·101	1·022	·329

Sodium Bromide.

Grm. eqv. per Litre.	Elev. of Boiling point.	$\frac{E}{\eta}$.
·10	·083	·83
·18	·159	·94
·64	·661	·94
1·12	1·118	·99
1·32	1·341	1·03
1·49	1·392	1·07
1·71	2·033	1·18
1·87	2·032	1·18
2·10	2·533	1·20
2·25	2·816	1·25
2·29	2·964	1·24

Aluminium Sulphate.

Grm. eqv. per Litre.	Elev. of Boiling point.	$\frac{E}{\eta}$.
·141	·081	·54
·860	·398	·46
4·34	2·132	·49
5·52	3·014	·54
6·50	4·298	·66
7·10	4·949	·70
7·22	5·314	·73
7·32	5·374	·73
7·46	5·608	·76
7·84	5·822	·74
8·34	6·258	·75

Potassium Iodide

grm. eqv. per litre.	Elev. of Boiling point.	$\frac{E}{\eta}$
.515	.394	.80
.849	.866	1.01
1.368	1.350	1.03
1.695	1.721	1.05
1.948	2.146	1.11
2.665	3.184	1.9
3.341	4.360	1.34
3.660	4.901	1.34
4.16	5.955	1.48
4.62	6.709	1.50

Sodium Chloride.

grm. eqv. per litre.	Elev. of Boiling point.	$\frac{E}{\eta}$
.203	.198	.94
1.38	1.332	.96
1.52	1.482	.94
1.58	1.619	1.02
1.84	1.842	1.01
2.08	2.132	1.02
2.26	2.313	1.02
2.44	2.551	1.04
2.52	2.684	1.06
2.62	2.818	1.04
2.70	2.936	1.08

Ammonium Chloride.

grm. eqv. per litre.	Elev. of Boiling point.	$\frac{E}{\eta}$
.141	.128	.90
1.055	.892	.84
1.852	1.662	.89
2.345	2.141	.92
2.844	2.750	.95
3.338	3.344	1.01
3.922	4.160	1.06
4.365	4.880	1.11
5.042	5.813	1.16
5.412	6.598	1.21
6.022	7.564	1.25
6.420	8.449	1.31

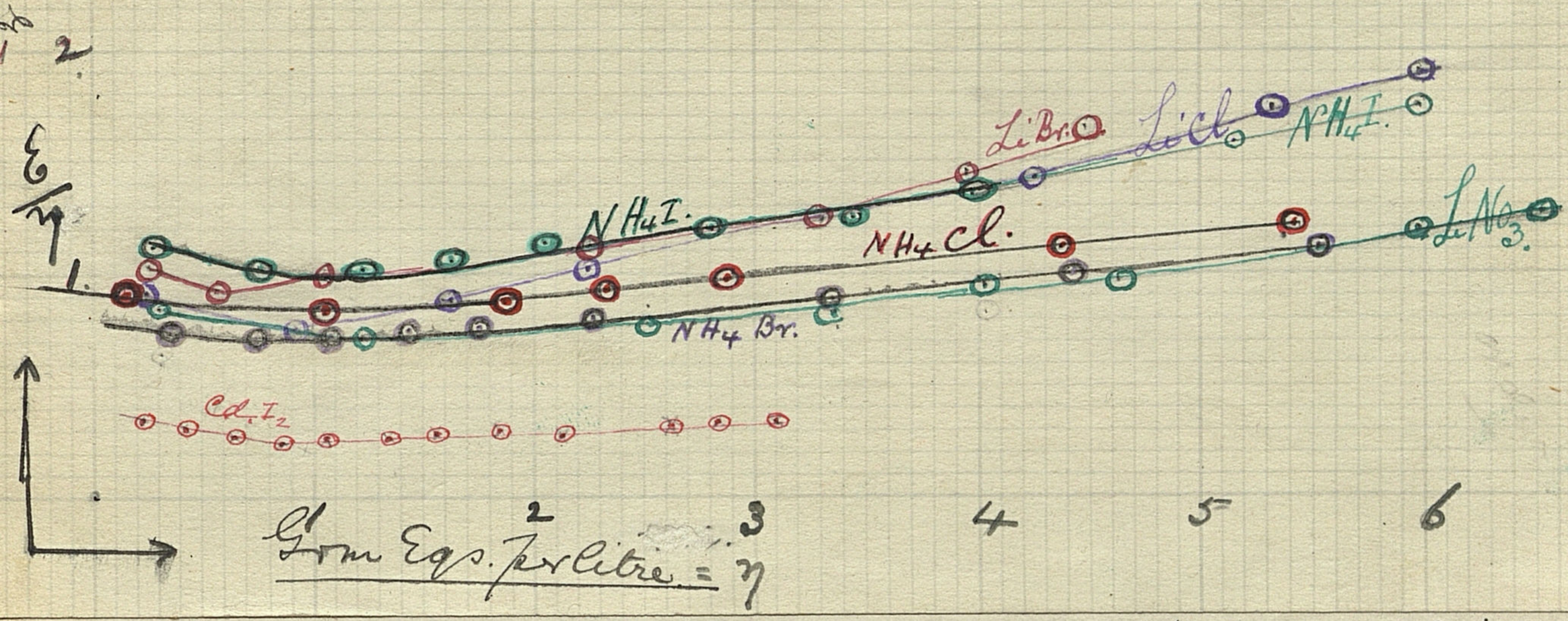
In these tables η = the number of grm. eqs. per litre.

Lithium Bromide.

Lithium Chloride.

Lithium Nitrate.

grm. eqs. per litre.	Elec. of Hadings point.	$\frac{E}{\eta}$	grm. eqs. per litre.	Elec. of Hadings point.	$\frac{E}{\eta}$	grm. eqs. per litre.	Elec. of Hadings point.	$\frac{E}{\eta}$
·262	·244	1·04	·250	·231	·92	·312	·264	·84
·584	·532	·91	·922	·743	·80	1·215	·841	·70
1·061	1·085	1·03	1·58	1·592	1·04	2·025	1·516	·75
1·260	1·428	1·13	2·23	2·547	1·14	2·788	2·241	·81
1·549	1·798	1·16	2·84	3·438	1·19	3·341	2·918	·86
2·243	2·695	1·20	3·60	4·649	1·29	4·118	3·921	·95
2·945	3·741	1·27	4·25	6·017	1·41	4·62	4·428	·96
3·286	4·369	1·33	4·70	7·542	1·60	5·39	6·160	1·14
3·94	5·765	1·46	5·31	9·294	1·75	5·98	7·200	1·20
4·48	7·421	1·65	5·98	11·419	1·90	6·52	8·496	1·28



commencing with the one nearest the ~~Ordinate~~ eq. axis

For the Lithium salts the order is $Li NO_3$ Li Cl Li Br.

Whereas for the Ammonia salts the ~~order~~ is Bromide, chloride Iodide. The hydration results which are given later differ correspondingly, their hydration order being different. from the other salts

So far as my results go, the Ammonia salts are unique in this respect. (their order) This may be due to their hydration or some other cause. It may be worthy of note that Biltz gives a somewhat strange curve for NH_4 on page 203 Zeit. phys Chemie 40, 1902.

The results obtained in part IV are given graphically in the curves given below.

---

1. I have plotted elevation against per centage composition, and against the grammes of salt added to a constant amount of solvent In the latter case the straightness of several of the curves even to high concentrations is noteworthy. This is particularly so for $Cd.I_2$, $(NH_4)_2$, So_4, NH_4I, NH_4Br, and Li No_3.
The same is true in a less degree of the curves for Na el. NaBr. and NH_4Cl and is still less of the curve for Li cl.

---

2. Gramme equivalents per litre have been plotted against gramme of combined solvent. Most of the curves are concave towards the gramme equivalent axis, but Na el is concave towards the grammes of solvent in combination axis. As a rule therefore the curves indicate a decreasing rate of increase of hydration at high concentrations.

---

3. Gramme equivalent elevation has been plotted against equivalent concentration. These curves give minimum points as a rule, and in several instances are approximately parallel to each other, the order commencing with the one nearest the gramme equivalent axis.

These minima are readily explained on the hydration theory. The minimum point is that at which the bending due to increase of ionization is equal to that due to decrease of hydration.

The convexity of the curve towards the gramme equivalent elevation axis being due to increase of ionization, and its concavity towards the same axis to increase of hydration having a greater influence than decrease of ionization.

---

4. /

4. Ionization has been plotted against the elevation constant. These curves show that to high concentrations a linear relation holds between ionization and the elevation constant. The line changing direction at a certain ionization. The curves for Li cl commences to bend at an ionization of about ·35.

These curves cannot but be of considerable interest from the standpoint of hydration, which will probably increase as hydration data are obtained. Should it so happen, as is probable that for several of these salts the hydration is both molecular and ionic the straightness of the curves for concentrated solutions would be interesting.

The bending of the curves for Li cl ~~would~~ might possibly be accounted for by a decrease in the rate of change of ionization were the hydration molecular and ionic as there would be more than two variables The bending ~~may therefore indicate~~ would be explained on the assumption* that the Li cl molecules hydrat which is ~~also~~ indicated by the salt being deliquescent and perhaps by the high hydration values which have been obtained for the salt

It is not supposed that in every instance the curves change direction so sharply as indicated by those drawn. The ionization at which the curve changes direction gives a means of determining at what ionization hydration commences and the corresponding concentrations may be obtained.

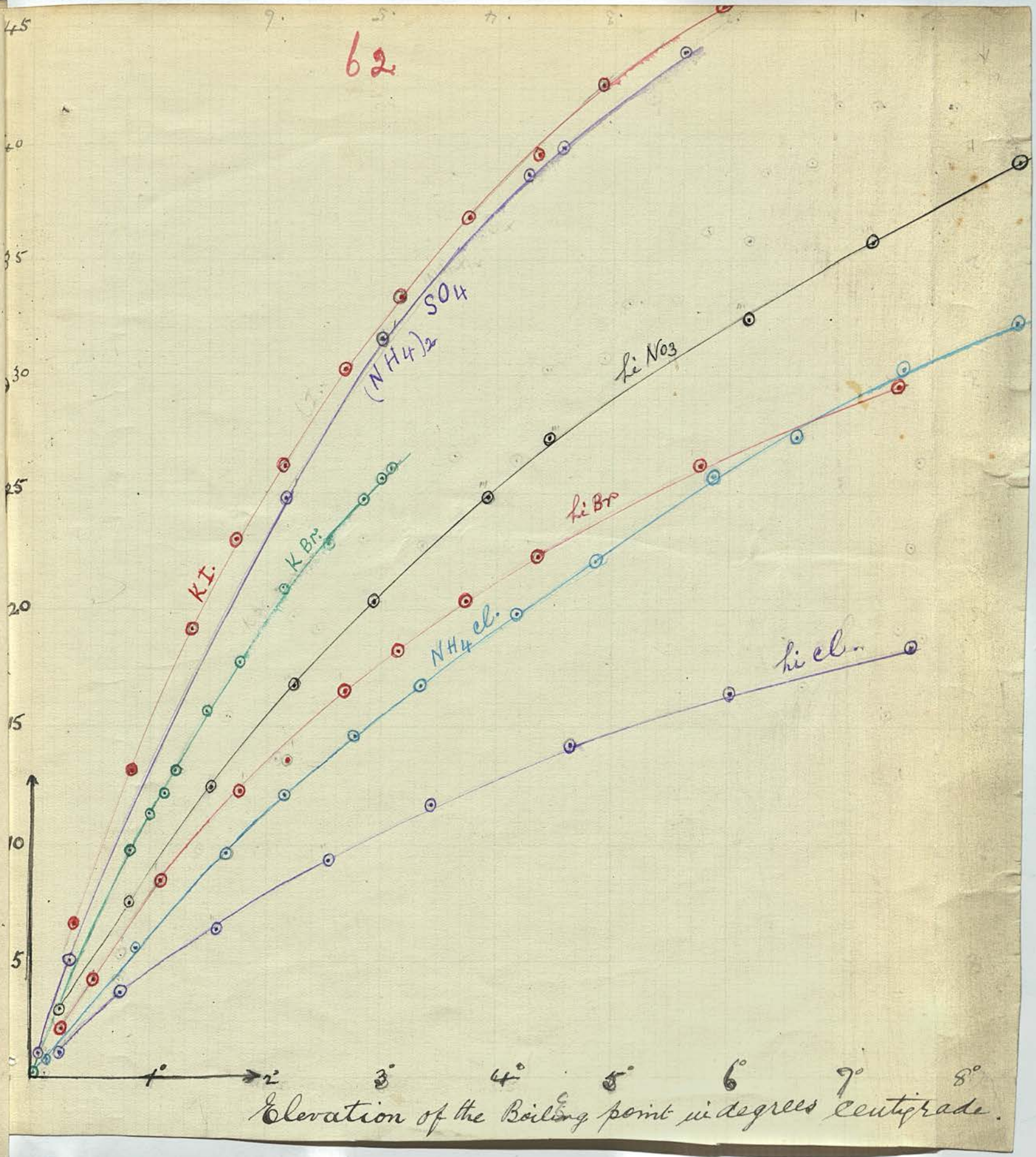
The following rough approximations for the commencement of hydration have been obtained in this way.

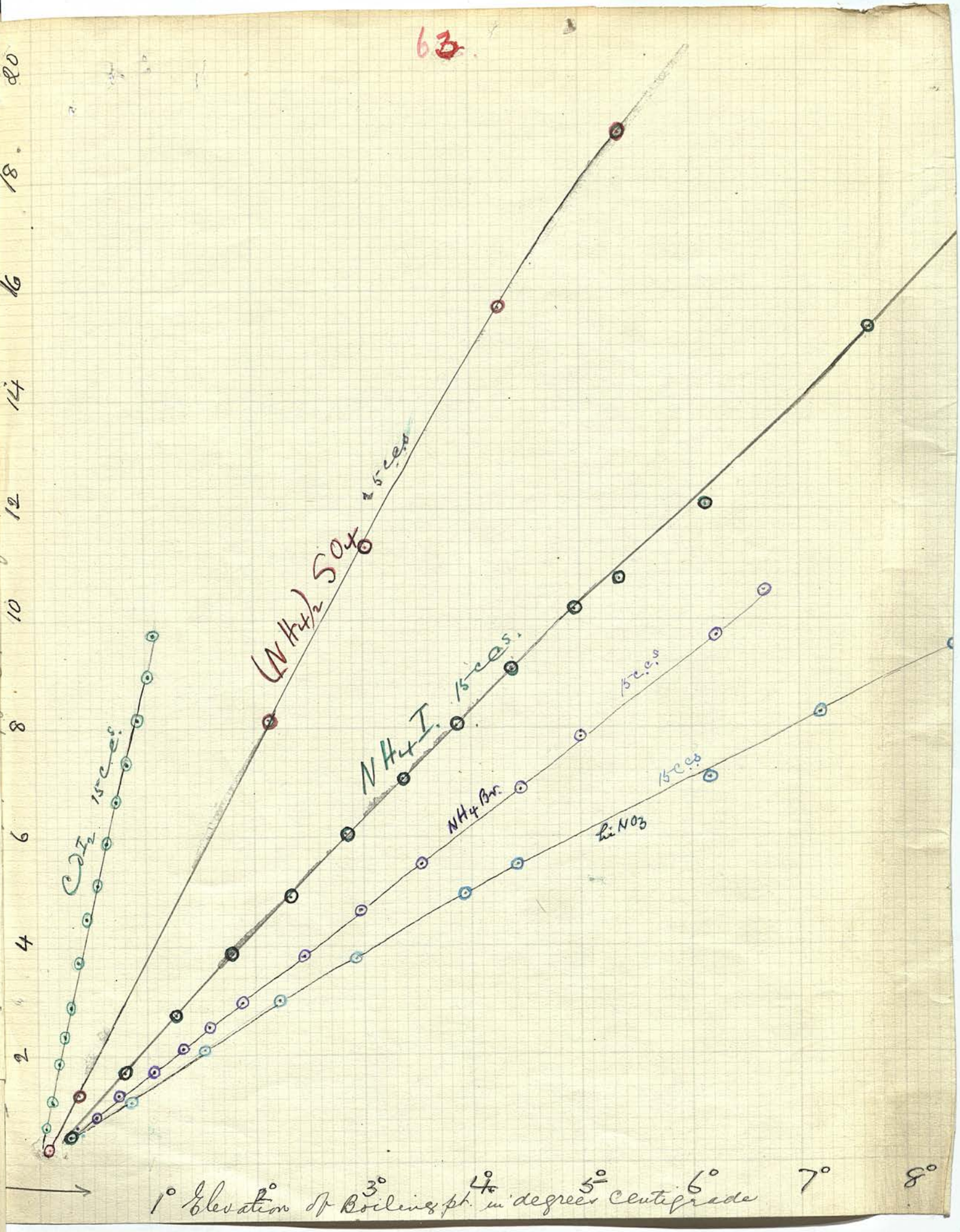
$Cd.I_2$ commences to hydrate at ~~1~~·8 gramme evuivalents per litre.

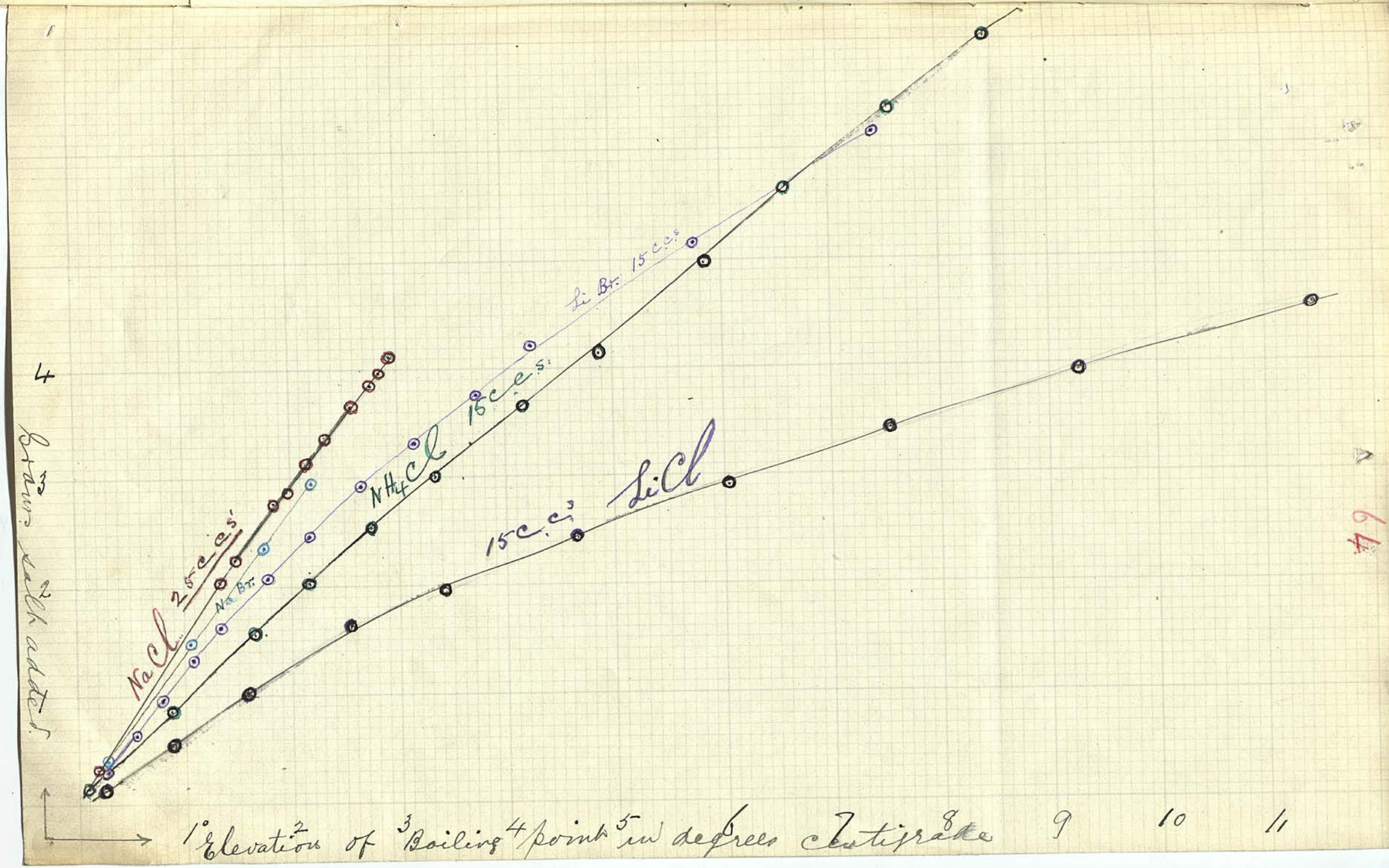
$LiNo_3$	"	"	"	"	1·0	"	"	"	"
NH_4cl	"	"	"	"	1·0	"	"	"	"
Li cl	"	"	"	"	·92	"	"	"	"
NH_4Br	"	"	"	"	·74	"	"	"	"
NH_4I.	"	"	"	"	.70	"	"	"	"

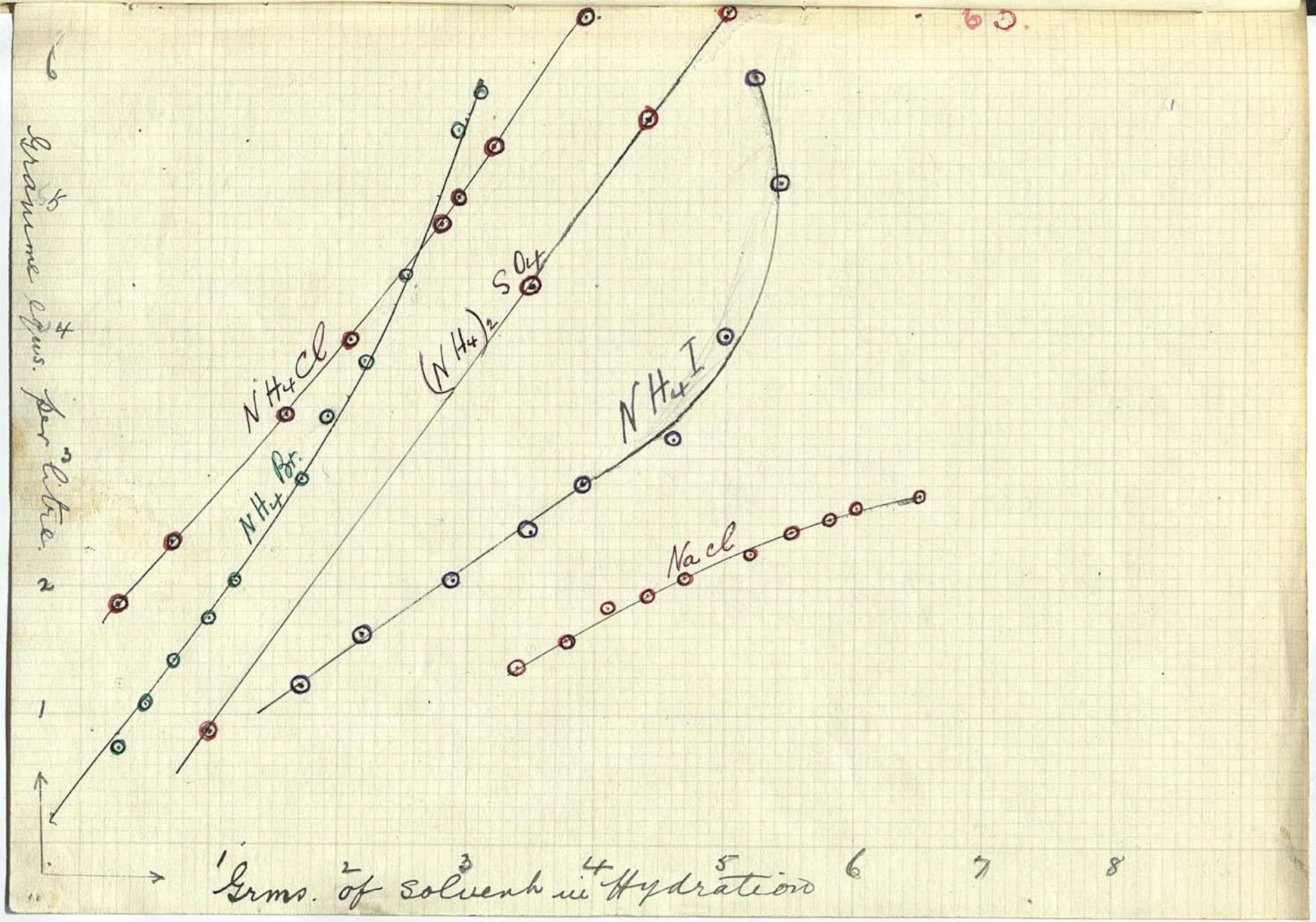
-----oOo-----

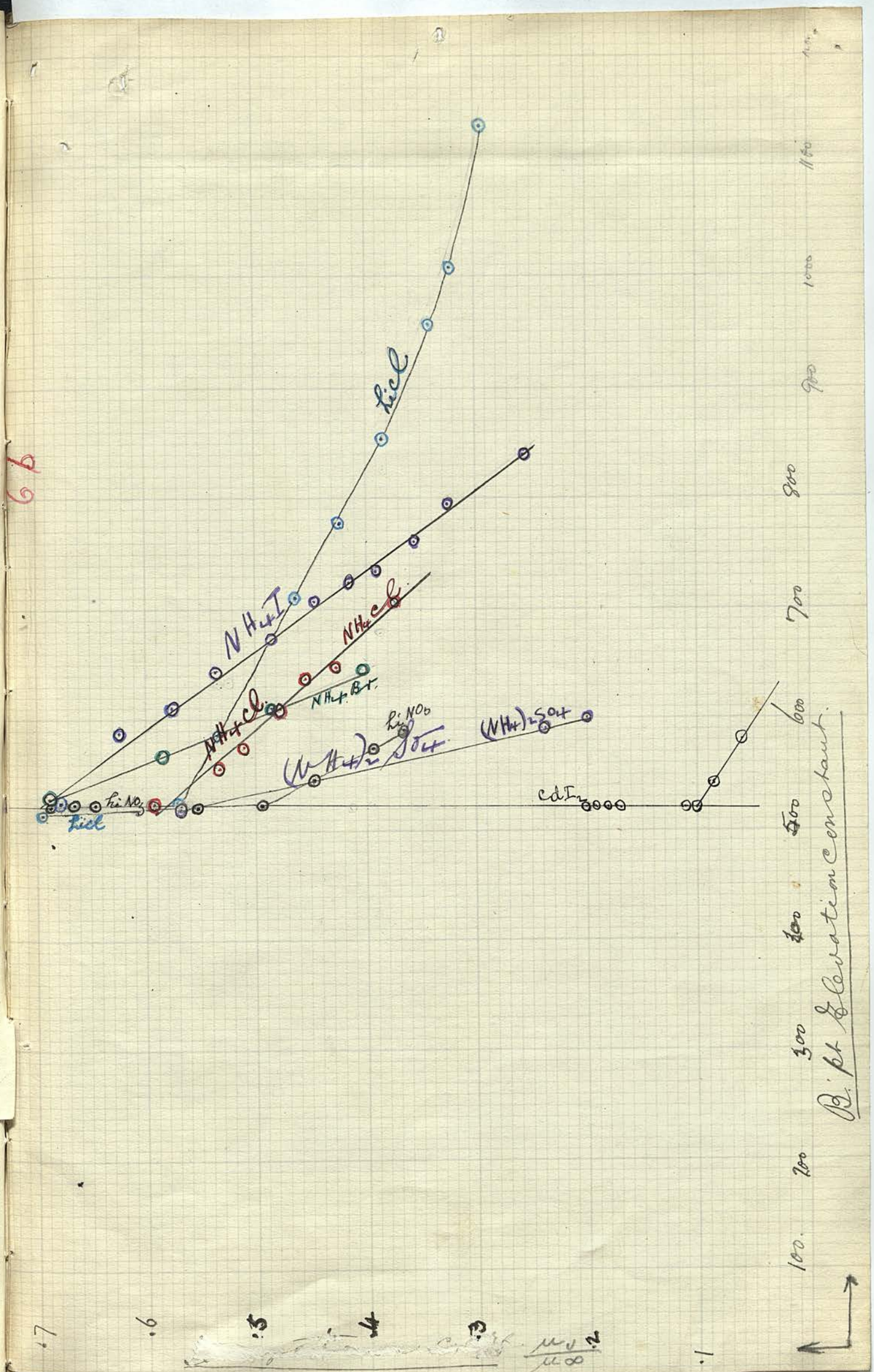
* It is not supposed that the bending may not be due to another cause.


45
40
35
30
25
20
15
10
5
1°
2°
3°
4°
5°
6°
7°
8°
KI.
(NH4)2 SO4
KBr.
Li NO3
Li Br
NH4 cl.
Li cl.
Elevation of the Boiling point in degrees Centigrade.

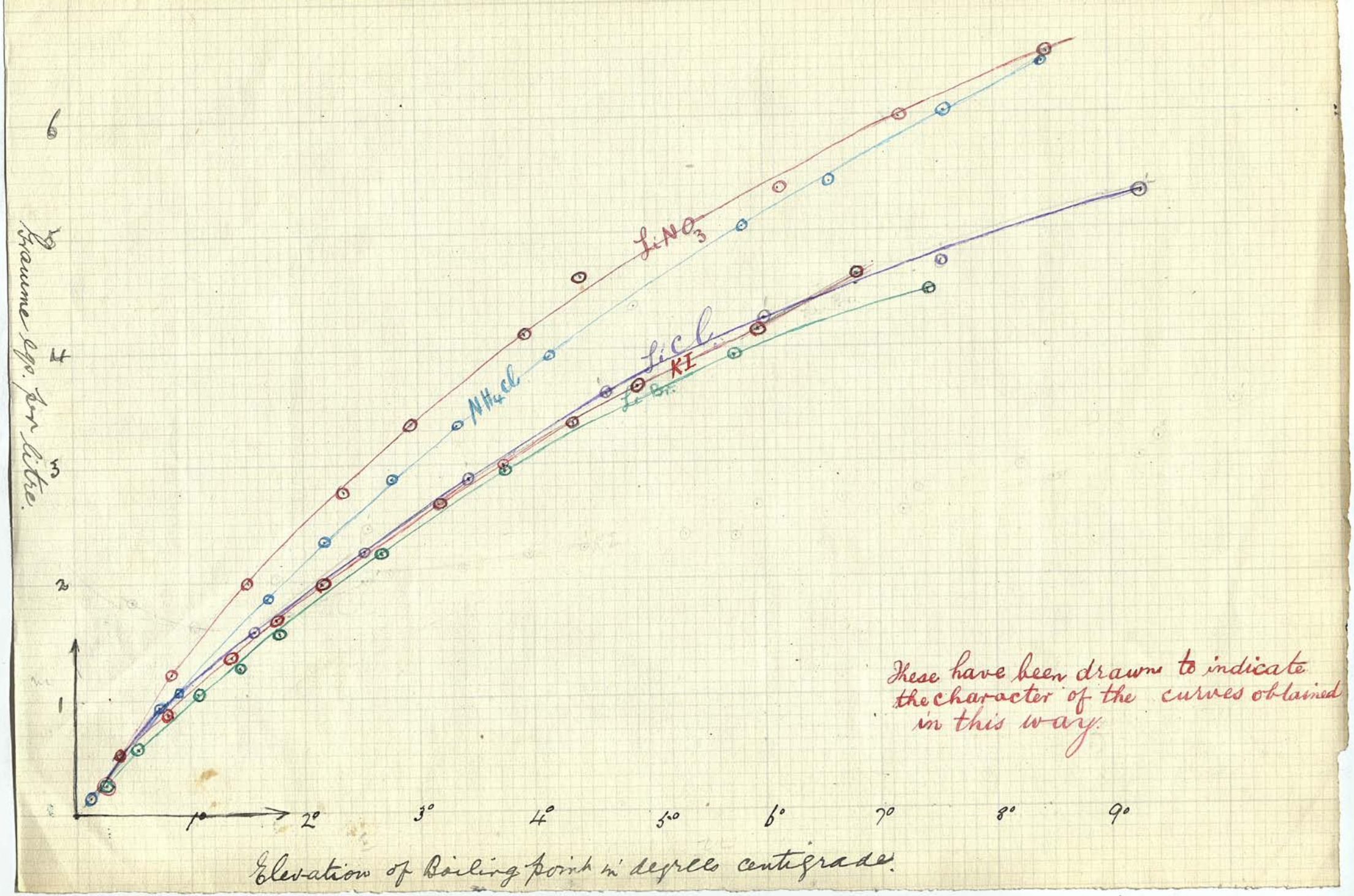

20
18
16
14
12
10
8
6
4
2
$(NH_4)_2SO_4$ 15 c.c.s.
NH_4I. 15 c.c.s.
NH_4Br. 15 c.c.s.
$LiNO_3$ 15 c.c.s.
CdI_2 15 c.c.s.
1° 2° 3° 4° 5° 6° 7° 8°
Elevation of Boiling pt. in degrees centigrade


NaCl 25 c.c.s.
Na Br. 15 c.c.s.
NH4Cl 15 c.c.s.
Li Br. 15 c.c.s.
LiCl 15 c.c.s.
Grams salt added.
1 2 3 4 5 6 7 8 9 10 11
Elevation of Boiling points in degrees Centigrade


Grams. of solvent in Hydration
Grams. of Salt per Litre.
1
2
3
4
5
6
7
8
NH4Cl
NH4 Br.
(NH4)2 SO4
NH4 I
Na Cl

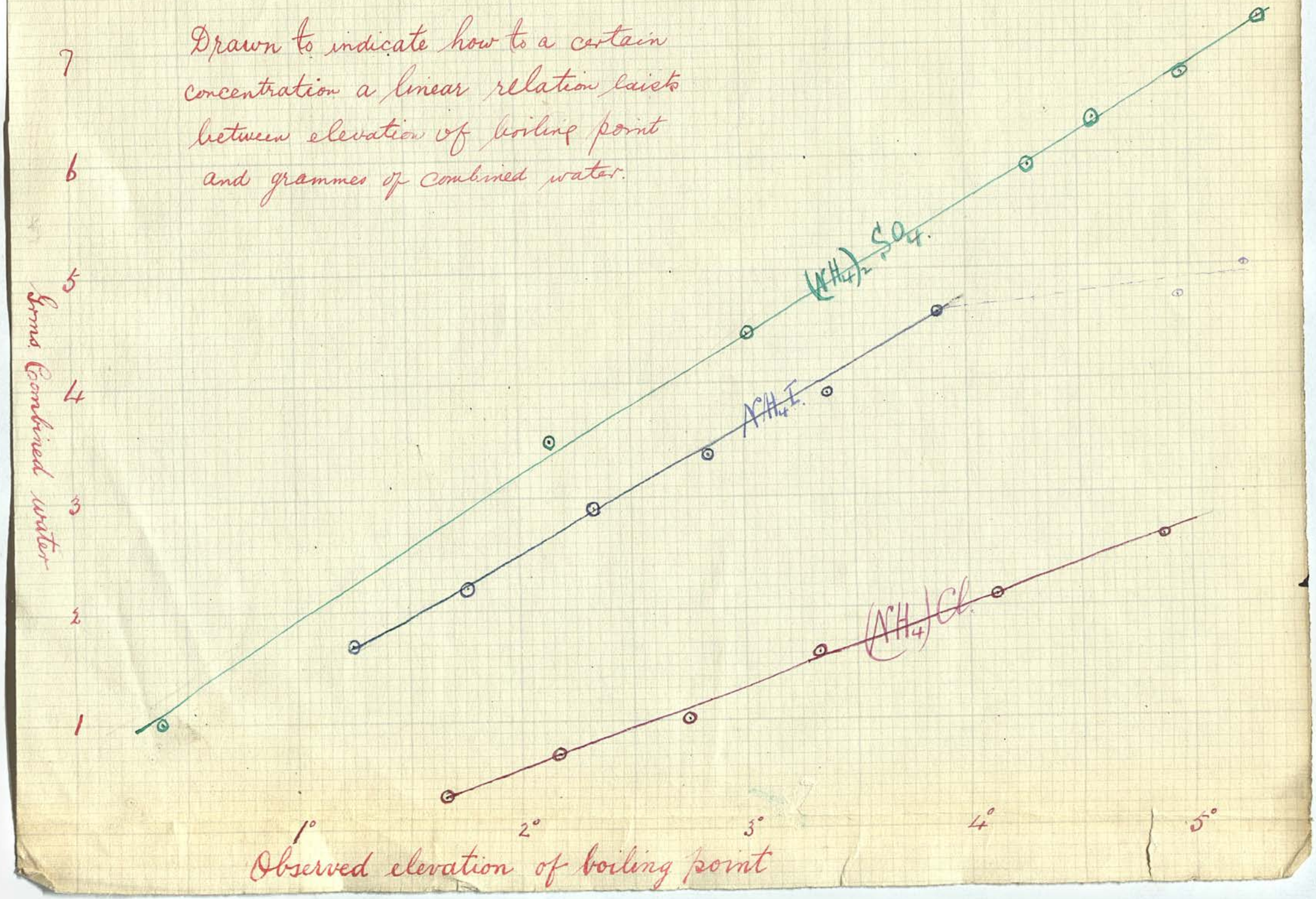


B. pt & concentration curve.



These have been drawn to indicate the character of the curves obtained in this way.

Drawn to indicate how to a certain concentration a linear relation exists between elevation of boiling point and grammes of combined water.



Resumè of results obtained.

1. A method has been brought forward giving increased accuracy in boiling point research.

2. A determination has been made of the so called boiling point constant for electroytes..

3. Molecular weight determinations have been made for several salts.

4. An improved method of obtaining conductivity values at the boiling point of the solvent has been given and apparatus described.

5. The results of research on concentrated solutions with a view to find out the meaning of the phenomenal values of C. for such solutions are given. Several theories being tested and finally these high values are ascribed to hydration.

6. The hydration figures obtained indicate that were association molecular alone, its amount quickly reaches a maximum and then decreases gradually for all concentrations. Where the hydration ionic, the maximum is reached gradually which is steady until high concentrations are reached and then it decreases.

Where the hydration that of both molecules and ions, a maximum is gradually reached which continues constant until considerable concentrations are reached, and then falls off gradually.

7. The results of an extensive research on hydration are given. The molecular, the ionic, and the molecular ionic theories being considered, and the conclusion arrived at that the ions hydrate, and probably the molecules also, in the case of deliquescent salts.

8. ~~Several ionic hydration calculations have been made on the basis of the theories to bring up five hundred of water and the ions are two and one half molecules.~~

9. The elevation of boiling point grammes of combined or associated water curves show that between elevation of boiling point and association a linear relation exists for all the salts considered.

10. The $\frac{\mu_1}{\mu_0} \frac{W_1}{W_0}$ boiling point elevation constant curves which have bee drawn, indicate that when hydration is not considered, a double linear relation holds, ~~for all concentrations~~ (LiCl bends at .35=D), the line changing direction /

direction when hydration comes on. By the aid of these, the io ionization at which hydration commences, might be accurately determined. The curves also indicate that the hydration comes on gradually, as might also be inferred from the symmetry of the elevation concentration curves which are given.

11. A comparison of curves numbered shows that the per centage composition ionization curves are the straightest.

12. The hydration theory being finally adopted, it explains the phenomenal values otherwise obtained for the elevation constant, as due to the shrinkage of the active water, owing to combination with salt particles, and not to variation of the so called constant. Presupposing this theory C. is constant, the value obtained is therefore that for all concentrations.

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Conclusion.

In conclusion a considerable number of series have been duplicate Those in part 1, to find out and are given to show the relation betwee one series and another for dilute solutions. In the other parts duplicationshad different meanings. In some instances, it was meant to test the accuracy of a series already obtained, in others to obtain a fuller view of the behaviour of the solutions of a salt. In these instances the one series is taken to high, the other to only moderate concentrations. In carrying out the experiments boiling tubes of thre different sizes were used, a 50 c.c. a 25 c.c. and a 15 c.c. tube.

In the tables the results obtained from different tubes in which different quantities of solvent were used have been placed one agains the other, but throughout there is the greatest harmony.

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